# A LABORATORY SCALE SYNTHESIS OF GEOPOLYMER FROM CONSTRUCTION WASTES



A THESIS SUBMITTED TO THE CENTRAL DEPARTMENT OF CHEMISTRY INSTITUTE OF SCIENCE AND TECHNOLOGY TRIBHUVAN UNIVERSITY NEPAL

> FOR THE AWARD OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

> > BY ARVIND PATHAK MAY 2016

### DECLARATION

Thesis entitled "A Laboratotry Scale Synthesis of Geopolymer from Construction Wastes" which is being submitted to the Central Department of Chemistry, Institute of Science and Technology (IOST), Tribhuvan University, Nepal for the award of the degree of Doctor of Philosophy (Ph.D.), is a research work carried out by me under the supervision of Professor Dr. Vinay Kumar Jha, Central Department of Chemistry, Tribhuvan University, Nepal.

This research is original and has not been submitted earlier in part or full in this or any other form to any university or institute, here or elsewhere, for the award of any degree.

Arvind Pathak

#### RECOMMENDATION

This is to certify that **Mr. Arvind Pathak** has completed Ph.D. thesis entitled "**A Laboratory Scale Synthesis of Geopolymer from Construction Wastes**" for the award of Doctor of Philosophy (Ph.D.) in **Chemistry** under my supervision. To my knowledge, this work has not been submitted for any other degree.

He has fulfilled all the requirements laid down by the Institute of Science and Technology (IOST), Tribhuvan University, Kirtipur for the submission of the thesis for the award of Ph.D. degree.

Professor Dr. Vinay Kumar Jha Supervisor Central Department of Chemistry Tribhuvan University, Kirtipur Kathmandu, Nepal

MAY 2016

त्रिभुवन विश्वविद्यालय TRIBHUVAN UNIVERSITY विज्ञान तथा प्रविधि अध्ययन संस्थान Institute of Science and Technology



कीर्तिपुर, काठमाडौं, नेपाल । Kirtipur, Kathmandu, NEPAL.

## रसायन शास्त्र केन्द्रीय विभाग CENTRAL DEPARTMENT OF CHEMISTRY

## **CERTIFICATE OF APPROVAL**

Date: May 9, 2016

On the recommendation of Prof. Dr. Vinay Kumar Jha, this Ph. D. thesis submitted by Mr. Arvind Pathak, entitled "A laboratory scale synthesis of geopolymer from construction wastes" is approved by Central Department Research Committee (CDRC) for the further processing.

**Dr. Megh Raj Pokhrel** Professor, Head, Central Department of Chemistry Tribhuvan University Kirtipur, Kathmandu Nepal

Tel.: +977-1-4332034, Fax No.: +977-1-4330537, http://www.cdctu.edu.np e-mail: info@cdctu.edu.np

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#### ABSTRACT

In the 21<sup>st</sup> century global warming becoming the most challenging problem, a huge amount of wastes are generated due to the rapid urbanization and construction of several new structures, renovation and demolition of old buildings especially in developing countries several million tons of construction and demolition wastes (CDW) globally. Much of the concrete waste from the construction industries is used as land filled, leading to environmental and ecological problems such as occupation of large areas of land, generation of dust, contamination of surface and underground water.

Recently in Nepal after Gorkha earthquake on April 25 and its aftershocks a total of 4,784 public and 531,266 private buildings were either destroyed or damaged. The amount of such a large waste is creating economic burden as well as environmental pollution. This disaster compelled us for the complete utilization of these wastes generated for sustainable development due to the diminishing natural resources.

Construction and demolition wastes are considered priority waste in European Union countries. As per Eurostat 2010, European Union generated 854.55 million tons of Construction and demolition waste. European Catalogue of Waste (ECW) has classified CDW in chapter 17 as Concrete (17 01 01), Bricks (17 01 02), Tiles and ceramics (17 01 03). The recycling of construction and demolition waste (CDW) is limited to the use of crushed aggregates in low-specification applications. Recycling and utilization of such waste would be a significant contribution to the environment and sustainable development towards the adoption of "zero waste" principle.

These wastes are rich in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which can be used as a raw material for the synthesis of geopolymer. One of the promising technology i.e., geopolymerisation has immense potential to convert such wastes into value added product. Geopolymerisation involves a chemical reaction between solid aluminosilicate oxides and alkaline activator solution at ambient or slightly elevated temperatures, resulting an amorphous to semi-crystalline polymeric structure with Si–O–Al and Si–O–Si bonds of high mechanical strength.

Four types of CDW were selected in this study. i.e., coal fly ash, demolished cement sand mixture, demolished cement sand concrete mixture and brick powder. Calorimetric analysis showed that brick dust is not very reactive. However the use of suitable additives, decrease in particle size of the raw material, appropriate ratio of activator solution, curing temperature and time enhances the mechanical properties of the geopolymer products.

The compressive strength values of the geopolymer products were ranges from 8.35 to 60.00 MPa (NaOH, 6M; particle size,  $\leq$ 53 µm and Na<sub>2</sub>SiO<sub>3</sub>/BD-K = 1.5) at 28 days of curing at ambient temperature (40 °C).

In case of temperature variation, the compressive strength values of the geopolymer products (BD-K2) found increasing from 9.40 to 23.47 MPa at 28 days of curing for 40 and 70 °C respectively for four hour followed by curing at room temperature ( $12\pm3$  °C).

At Si/Al ratio equal to 3.16, the compressive strength values were found to be maximum, with the further increase in the ratio, the compressive strength values were found to be decreasing. A similar trend of result was found from the plot of compressive strength against  $SiO_2/Al_2O_3$  mass ratio. A maximum compressive strength was found at Na<sub>2</sub>O/SiO<sub>2</sub> mass ratio equal to 0.58, below this ratio the compressive strength found to decrease. A lower Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio was found favorable, a maximum compressive strength was found at Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 0.23.

The properties of geopolymers are found comparable with that of equivalent building materials. The structural changes in resulting geopolymer were studied using XRD, FTIR and SEM-EDX. The present study describes briefly the potential of geopolymer technology towards green buildings and future sustainable with a reduced carbon footprint. Such geopolymers can be used as a building material which can reduce the greenhouse gas emission as well as reduce the depletion of natural resources.

# **Keywords:** Alkaline activator; Compressive strength; Construction and demolition waste; Geopolymerisation; Global warming.

# LIST OF ABBREVIATIONS

CFA	Coal fly ash
DCSM	Demolished cement sand mixture
DCSCM	Demolished cement sand concrete mixture
SCM	Sand cement mixture
BD-K	Brick dust of Kathmandu
BD-J	Brick dust of Jamshedpur
BDAM	Brick dust alkali mixture
BDMK	Brick dust metakaolin
BDL	Brick dust lime
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron micrograph
EDX	Energy dispersive X-ray
MPa	Mega Pascal
psi	Pound-force per square inch
MW	Megawatt
°C	Degree centigrade

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# CHAPTER 1 INTRODUCTION

#### 1.1 Background

Solid wastes are any discarded or abandoned materials. Solid wastes can be solid, liquid, or semi-solid material. Municipal solid wastes is often described as the waste that is produced from residential and industrial, commercial and institutional sources with the exception of hazardous and universal wastes, construction and demolition wastes (Tchobanoglous and Kreith, 2002).

Municipal solid waste (MSW) includes garbage, refuse, sludge, rubbish, tailings, debris, litter and other discarded materials resulting from residential, commercial, institutional and industrial activities which are commonly accepted at a municipal solid waste management facility, but excludes wastes from industrial activities regulated by an approval issued under the Nova Scotia Environment Act (Solid Waste-Resource Management Regulations, 1996). Hazardous waste is so called due to its nature and quantity are potentially hazardous to human health and/or the environment and which require special disposal techniques to eliminate or reduce the hazard (Meakin, 1992). Universal Waste is the waste which poses significant environmental and safety hazards which cannot be processed with standard MSW, but does not pose the same level of risk as hazardous wastes. Construction and demolition wastes, which is generated whenever construction and demolition activities take place such as building roads, bridges, fly over, subway, remodeling etc. those adversely affecting the environment led to serious management problems in cities and countries (Rodriguez et al., 2007)

According to European waste catalogue, construction and demolition waste has been classified as 17 01 concrete, bricks, tiles, ceramics (European Commission Report, 1999).

17 01 01	Concrete
17 01 02	Bricks
17 01 03	Tiles and ceramics
17 01 06	Mixtures or separate fractions of concrete, bricks, tiles and
	ceramics containing dangerous substances
17 01 07	Mixture of concrete, bricks, tiles and ceramics other than those
	mentioned in 17 01 06

Population growth, increasing urbanization, industrialization, rising standards of living due to technological innovations have contributed to an increase in the quantity of construction and demolition wastes that could be a significant source in the reduction of using natural resources. There is a lack of significant knowledge regarding the volume generated, their corresponding impact, social cost involved and its reuse potential. In general, the waste generation during construction is estimated to 40 to 60 kg/m<sup>2</sup>. Similarly, waste generation during renovation and repair work is estimated to be 40 to 50 kg/m<sup>2</sup>. The highest contribution to waste generation between 300 to 500 kg/m<sup>2</sup> of waste from the partial and complete demolition of buildings, respectively (http://www.waste-management-world.com/articles/print/volume-12/issue-5).

Concrete is the most widely used construction material in the world. Ordinary Portland cement (OPC) has traditionally been used as the binder material in concrete. During Cement production, calcium carbonate (CaCO<sub>3</sub>) is heated in a kiln at a temperature of approximately 1400 °C, thus breaking the calcium carbonate into lime (CaO) and carbon dioxide (CO<sub>2</sub>) in a process which is known as calcination.

$$5CaCO_3 + 2SiO_2 \rightarrow (3CaO, SiO_2) (2CaO, SiO_2) + 5CO_2$$

This  $CO_2$  is emitted to the atmosphere and silica-containing materials are added to the lime to produce the intermediate product, clinker. The clinker is then allowed to cool and is mixed with a small amount of gypsum to produce Ordinary Portland Cement (EPA, 2014). The large amount of energy required to drive this process are generated by the combustion of fossil fuels, which results in green house gas (GHG) process energy emissions. Additionally, fossil fuels are also required to extract and refine the fuels used in the cement manufacturing process. With the advancement of technology, production of alternative cements to OPC reduces greenhouse gas emissions ranges from 0.66 to 0.82 kg of  $CO_2$  for every kilogram of cement production which is approximately contributed 5–7% of global anthropogenic  $CO_2$  emissions (Pithadiya and Nakum, 2015; Turner, 2013 and Zivica et al., 2014). However the production of geopolymeric cement requires about 60% less energy and emits three times less  $CO_2$  compared to OPC (Yip et al., 2004 and Van Deventer et al., 2006).

#### Fly ash (FA)

Fly ash is generated as a byproduct of coal combustion residue mainly of thermal power plants. Such fly ash has been regarded as a problematic solid waste all over the world. The most common waste management option for fly ash in the United States is landfill storage. It is non-biodegrade in anaerobic conditions and therefore does not generate any  $CH_4$  emissions in the landfill environment, store carbon in the landfill or generate any avoided utility emissions. Also transportation of fly ash to a landfill and operation of landfill equipment results in anthropogenic CO<sub>2</sub> emissions (EPRI, 1998).



Figure 1.1: Fly ash deposited from thermal power plant.

Most of the elements below atomic number 92 are present in coal fly ash. A 500 MW thermal power plant releases 200 million tones  $SO_2$ , 70 tones  $NO_2$  and 500 tones fly ash approximately every day. Particulate matter (PM) considered as a source of air pollution constitutes fly ash. The fine particles of fly ash reach the pulmonary region of the lungs and remain there for long period of time; they behave like cumulative poisons. The submicron particles enter deeper into the lungs and are deposited on the alveolar walls where the metals could be transferred to the blood plasma across the cell membrane. The residual particles being silica (40–73%) cause silicosis (Senapati, 2011).

Fly ash requires a large area of land for disposal. Toxicity associated with heavy metals such as As, Ba, Hg, Cr, Ni, V, Pb, Zn and Se leached to groundwater as well as drinking water supplies (EPRI, 1998; Mattigod, 1990 and Senapati, 2011). Fly ash, being treated as waste and a source of air and water pollution till recent past, is in fact a resource

material and has also proven its worth over a period of time (Dwivedi et al., 2014). Fly ash production in major countries is shown in the following Figure 1.2 (ACAA, 2013; CEA report 2014 and Dhadse, 2008):



Figure 1.2: Fly ash production (million tones/year) in different countries

Increasing worldwide concern for environmental protection, growing economical constraints and depleting natural resources has led many research institutions to look into the possibility of an integrated material cycle. Waste utilization is based on the notion that *waste is a resource, but at wrong place*. Realizing this concept many new technologies such as clean technology, zero waste products etc. have emerged, but these are still at the conceptual stage and waste generation is a ground reality.

During the last 30 years, extensive researches have been carried out to utilize the fly ash in various sectors, as this is not considered as hazardous waste. Broadly, fly ash utilization programs can be viewed from two angles, i.e. mitigating environmental effects and addressing disposal problems (Senapati, 2011). Fly ash utilization in major countries is shown in the following Figure 1.3 (ACAA, 2013, CEA report 2014 and Dhadse, 2008):



Figure 1.3: Utilization (%) of total produced fly ash in different countries.

Followings are some of the potential areas of use of the fly ash (Senapati, 2011):

Development of fly ash based polymer composites as wood substitute, fly ash based cement, bio-amelioration of fly ash on soil, fly ash bricks, fly ash in distemper, ceramics, ready mixed fly ash concrete, mine fills, roller compacted concrete and Asphalt concrete etc.

Fly ash, an artificial pozzolanic material are used in production of Portland Pozzalona Cements (PPC), as partly replacement of cement in mortar and concrete. Such building units have high strength, low heat of hydration, low permeability and hence more durability (Nawaz, 2013). Primarily fly ash is being used as an additive in concrete and cement, but high valued utilization of fly ash is being undertaken, such as producing geoplymer or inorganic fiber had shown a promising prospect (Tang et al., 2013).

In Nepal, there is no thermal power plant to generate electricity. The coal used in our country are mostly in cases of producing brick, thus the coal fly ash obtained from brick industries was considered as construction waste in this study.

#### Slag

Slag is a by-product generated during manufacturing of pig iron and steel in largest quantities. The disposal of such large quantities of slags becomes a major environmental concern and a critical issue for steel makers. It is produced by action of various fluxes upon gangue materials within the iron ore during the process of pig iron making in blast furnace and steel manufacturing. The slag produced at blast furnace (BF) during pig iron manufacturing is called blast furnace slag. The slag produced at steel melting shop is known as steel slag. Primarily, the slag consists of calcium, magnesium, manganese and aluminum silicates in various combinations together with iron oxide. The major basic difference between blast furnace slag and steel slag are iron content. In blast furnace slag, FeO is around 0.5%, whereas, in case of steel slag, total iron content varies from 16 to 23% (IMY, 2014).

In an integrated steel plant, 2 - 4 tons of wastes (including solid, liquid and gas) are generated for every ton of steel produced. The steel stockpiles shown in Figure 1.4 (Pajgade and Thakur, 2013).



Figure 1.4: Stockpiling of steel slag aggregates at Steel Industry, Wardha (Source: CEA report 2014)

Slag is mainly used in the cement manufacture and in other unorganized work, such as, landfills and railway ballast. A small quantity is also used by the glass industry for making slag wool fibers (IMY, 2014).

#### **Construction and demolition waste**

Construction and demolition waste (CDW) is a priority waste in European Union countries. It is emerging as one of the major waste worldwide. Reuse of CDW is getting increased attention as it is mainly waste of urban areas where almost no land is available for disposal. The major fraction of CDW comprises about 70% of total CDW are coal fly ash, demolished sand cement mixture (includes hydrated cement and sand), demolished sand cement concrete mixture (includes hydrated cement, sand, aggregate etc.), brick, tiles etc. and rest of 30% includes wood, metals, plastics, glass etc.

Recently in Nepal after Gorkha earthquake on April 25 and its aftershocks a total of 4,784 public and 531,266 private buildings were either destroyed or damaged as reported by Ministry of Home Affairs, Nepal (http://www.ekantipur.com/2015/06/02). Thus from these renovation activity huge amount of wastes will be generated that requires sustainable solution.



**Figure 1.5**: Construction and demolition wastes (a) generated (b) deposited (Source: http://www.fotosearch.com/photos-images/demolition.html; CEA report 2014)

The construction and demolition waste consists of two major fractions: concrete and ceramics. The major constituents of concrete are  $SiO_2$  and CaO along with minor concentration of  $Al_2O_3$  and  $Fe_2O_3$  mostly in crystalline phase. The main constituents of ceramic are  $SiO_2$  and  $Al_2O_3$  in crystalline and glassy phase (Rapazote et al., 2011).

The construction and demolition waste has become a global concern that requires sustainable solution. There is a significant potential for recycling and reutilizing construction and demolition waste for the use in value added applications and provides an alternative construction materials to maximize economic and environmental benefits. This would also contribute to control and reduction of the release of undesirable gases and pollutants to the environment. Recycling potential of solid waste such as construction debris, marble processing into building material has been studied (Pappu et al., 2007). However, some quantity of such waste is being recycled and utilized in building materials, dust is usually dumped on the riverbeds and this possesses a major environmental concern. In dry season, the marble powder/dust dangles in the air, flies and deposits on vegetation and crop. All these significantly affect the environment and local ecosystems. Fine particles result in poor fertility of the soil due to increase in alkalinity (Pappu et al., 2007).

For the protection of natural resources, prevention of environmental pollution and contribution to the economy by using waste material, a key strategy of construction waste management, recycling could offer the following benefits (Kartam et al., 2004 and Tam, 2008):

- (1) Reducing the demand for new resources,
- (2) Cutting down on transport and production energy cost,
- (3) Utilizing waste which would otherwise be lost to landfill sites,
- (4) Preserving areas of land for future urban development and
- (5) Improving the general state of the environment.

Rapid population growth and urbanization in developing countries have led to generate the large quantities of solid wastes and consequential environmental degradation. Around 90-95% of all waste in the world is land filled or disposed in open dumps, creating considerable nuisance and environmental problems due to lack of technical knowledge, financial and human resources as well as the existing policies (AIT, 2004). However construction and demolition debris is limited to use in low specification values i.e., land filling as well as separated into recyclable materials. One of the promising technologies, Geopolymerisation can be used to utilize the construction and demolition waste completely.

Geopolymerisation is emerging as an energy efficient and ecofriendly process to develop building materials from varieties of waste. Ceramic waste, which is alumino-silicate in composition, can be used as potential feedstock for geopolymer synthesis. The alkaline activation of construction and demolition waste is a chemical process that allows transforming glassy structures (partially or totally amorphous) into well compact cemented composites.

Geopolymerisation is a relatively new technology that transforms aluminosilicate materials into geopolymer, which involves a chemical reaction between solid aluminosilicate oxides and an alkaline activation solution at ambient or slightly elevated temperatures, yielding an amorphous to semi-crystalline polymeric structure with Si–O–Al and Si–O–Si bonds (Davidovits, 1988, 1991, 1994a and 1999; Duxson et al., 2007 and Majidi, 2009).

Geopolymers are made from a silica-alumina source, such as fly ash, metakaolin, blast furnace slag and a strong alkali activator, such as sodium hydroxide, water glass, potassium hydroxide, sodium sulphate, lime or combinations thereof. It has excellent strength and is often applied for waste stabilization purposes, encapsulation of heavy metals and for refractory purposes (Berger et al., 2009; Duxson et al., 2007; Provis et al., 2009 and Zhang et al., 2008).

The final product is a very hard ceramic like product that can be used for civil engineering applications such as blocks, precast concrete blocks and retaining walls similar to plain concrete (Rapazote et al., 2011). Study on the potential of geopolymer technology towards green buildings and future sustainable cities by utilizing several wastes or by-products, such as coal combustion ashes, metallurgical slag, construction and demolition wastes for the production of geopolymer concrete and construction component have been made (Komnitsas, 2011).

Inorganic polymers can be classified on the basis of their composition or their network connectivity. Depending upon the chemical structure, inorganic polymers can be divided into three basic types (Challa, 1993):

 (i) Homoatomic polymers: This type of polymer comprise of one kind of atom in the main chains. For example polymeric sulphur.

(ii) Heteroatomic polymers: This type of polymer consists of more than one type of atom in the main chains. For example hydrocarbon group (R)

Poly(siloxanes)	R   - Si- O	R   	R   ) - Si-(	)-
	 R	R	 R	
Poly(sulphurnide)	-N-S	= N - S	= N - S	. –

(iii) **Hybrid heteroatomic polymers:** This type of polymer consists of alternate inorganic atoms with typical organic units. For example

Poly(phenylene suphide)



The bonds between the main chain atoms of inorganic homo or heteroatomic polymers are predominantly covalent. These inorganic polymers show improved properties such as better heat and chemical stability.

Another way of classification is based on coordination number. All silica glasses can be viewed as the derivatives of the parent network present in amorphous silica. The connectivity of parent network is defined as the number of network bonds that link each repeated unit in the network. Silica contains the repeated unit of  $SiO_4$  (tetrahedral) has a connectivity of 4, but boric oxide contains the repeated unit of  $BO_3$  (trigonal) has a connectivity of 3 and a linear polymer such as polymeric sulphur has a connectivity of 2 (Ray, 1978).

#### **1.2** Statement of Problems

Construction and demolition waste is a byproduct during construction and demolition activities. It comprises of about 70 percent that includes concrete, masonry, tiles and ceramic waste and are not being currently recycled (EEA, 2010).

Due to environmental degradation and uncontrolled use of natural resources in the civil construction area, natural aggregates are becoming increasingly scarce and their production and shipment are becoming more difficult. Preventing the depletion of natural resources and enhancing the usage of waste materials has become a challenge. Environmental destruction and global warming have become the major issue in recent years. Use of more environmental- friendly materials is of paramount importance.

The production of OPC is accompanied by the emission of  $CO_2$ . One tone of cement production requires two tones of limestone, directly generates 0.55 tone of  $CO_2$  and yields an addition 0.40 tone due to the combustion of carbon fuel. Thus production of Portland cement is becoming less acceptable due the consumption of resource and biodiversity preservation and climate change. These novel geopolymers have unique property and are superior to conventional cements and hence substantially reduce  $CO_2$ emission caused by the cement industries (Davidovits, 1991, 1994a and 1994b).

Projections for building material requirement by the housing sector indicate a shortage of aggregates. There is a huge demand for aggregates in the housing and road sectors, but there is a significant gap in demand and supply. Analysis shows that reuse of construction waste can reduce the cost of low budget houses by approximately 30 to 35% without compromising the durability of the structure (http://www.waste-management-world.com/articles/print/volume-12/issue-5). Increased public opposition and growing cost of waste disposal which increases the cost of production, industries are under tremendous pressure. Also increasing concern worldwide for environmental protection, growing economical constraints and depleting natural resources have led to look into the possibility of an integrated material cycle. Many new concepts such as clean technology, zero waste products etc have emerged, but these are still at the conceptual stage and waste generation problem is the reality of present stage.

#### 1.3 Objectives of the Study

#### **1.3.1** General objectives

Solid wastes are generated annually from construction industries in significant amount, which include wasted sand, gravel, bitumen, bricks and masonry concrete. Globally, some quantity of such waste is being recycled and utilized in building materials (Asolekar, 2004). Therefore, concrete recycling is very important for sustainable development (Oikonomou, 2005).

There is no scientific method followed at the disposal sites, where waste is disposed without any processing. In addition, the nature of the system, constraints of space for storage of the construction and demolition wastes and lack of space for landfill are also important areas of concern (www.cseindia.org).

The aim of present study is based on recycling and complete utilization of construction and demolition waste through scientific understanding on the geopolymerisation behavior of CDW and to investigate the factors influencing the strength development. This knowledge will also be helpful in developing process for making building materials from construction and demolition wastes (CDW) that could reduce dependency on the limited natural resources to some extent. This new concept of waste utilization is an attempt to change in attitude towards waste as a resource. The environmental benefits of thus proposed geopolymer from CDW include:

- (i) Use of construction and demolition waste materials that would otherwise be land filled,
- (ii) Substantial reduction in environmental disruption and
- (iii) To offer a solution to reduce CO<sub>2</sub> emissions significantly by providing alternate to conventional cement materials.

#### **1.3.2** Specific objectives

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). Therefore, the study is aimed at the complete utilization of construction and demolition waste (CDW) and the main objectives of this research are:

- 1. To study the geopolymerisation behaviour of construction and demolition wastes such as coal fly ash, demolished sand cement mixture, demolished sand cement concrete mixture and brick.
- 2. To study and optimize the parameters such as alkali concentration, particle size, activator solution and curing time in the synthesis of geopolymer.
- To study the microstructural development using SEM-EDX, XRD and FTIR analysis.

CHAPTER 2 LITERATURE REVIEW

#### 2.1 Introduction

Various catastrophic fires and specially the incident such as the Summerland disaster on the Isle of Man in 1973 have caused great concern about the safety of structures in which plastics are extensively used (Ray, 1978). Also the raw material dependency for plastics is fossil carbon sources, which is limited. These facts forced to conduct research for the development of alternative materials that can be derived from unlimited mineral resources and ultimately synthesized inorganic polymer of desired physical and mechanical properties. Inorganic polymer refers to a substance composed of a network of atoms have mainly Si, Al, O instead of a backbone of carbon atoms. The substance includes siloxanes. silicates. polyphosphate, polysilanes, aluminosilicates. polyphosphazenes and polymeric sulphur nitride. Since 1960s, scientists have synthesized zeolites and feldspathoids similar to those found in nature by the integration of silica and alumina. Cement has also been regarded as a synthetic inorganic polymer due to its setting in the form of polycondensation (Challa, 1993 and Ray, 1978).

Geopolymer is extremely environmentally attractive for various reasons. Its performance as construction materials can be compared with Portland cement in lots of ways even though it needs no heat in its manufacturing process. This implies a substantial benefit with regards to reducing global CO<sub>2</sub> emissions and low energy consumption. Furthermore, the utilization of industrial by-products meets the increasing trend towards waste re-utilization (Jiminez et al., 2004). Geopolymer is an alumino-silicate material which includes excellent physical and chemical properties of numerous applications (Komnitsas and Zaharaki, 2007).

In ancient structures such as Pyramids in Egypt were built by casting the blocks and allowed to set, which then created an artificial zeolitic rock. Form experimental investigation, it has been rediscovered a new family of mineral binders named 'geopolymer' as it had the similarities with organic condensation polymers (Davidovits, 1994c; Davidovits and Morris, 1998 and Van Jaarsveld et al., 1996). In recent years, the development of the geopolymers has attracted great attention as an alternative for energy saving, environmentally friendly, durable and higher performing cement materials than
today's Portland cement (Davidovits, 1994a, 1994b; Duxson, et al., 2007 and Glasser, 1995).

Geopolymer binder can be used for applications to fully or partially replace OPC with environmental and technical benefits, including an 80 - 90% reduction in  $CO_2$  emissions and improved resistance to high temperature and aggressive chemicals (Rapazote et al., 2011). Attempt had been made to use fly ash from coal-fired power plant at Carolina to investigate the suitability in producing geopolymer binder to replace Ordinary Portland Cement binder in concrete application (Akbari et al., 2015).

The hardening process of cement and geopolymer is shown the following Figure 2.1:



Figure 2.1: Hydration process in Portland cement and geopolymer

In Portland cement hardening occurs through simple hydration of Calcium Silicate into Calcium Di-Silicate hydrate (CSH) and lime  $Ca(OH)_2$  (Davidovits, 2013). However in geopolymer, hardening occurs through poly-condensation of sodium/potassium oligo-(sialate-siloxo) into sodium/potassium poly(sialate-siloxo) cross linked network.

In comparison with traditional concrete, most of the studies confirmed that gepolymer is the innovation of waste-based concrete and consumes less energy and geopolymer cement are superior than that of ordinary Portland cement (Davidovits, 1991 and 1994c).

# 2.2 Historical Development of Geopolymer

The term "geopolymers" was coined by Davidovits in 1972 to the three-dimentional (3D) silico-aluminate materials called geopolymer (mineral polymers resulting from geochemistry or geosynthesis) (Davidovits, 2011). The three linear oligomeric building units, called 'polysialates' (Davidovits, 1991).

Geopolymer technology is considered new, but the technology has ancient roots and has been postulated as the building material used in the construction of the pyramids at Giza, Egypt shown in Figure 2.2 as well as in other ancient constructions (Barsoum and Ganguly, 2006; Davidovits, 1984, and 2008).



Figure 2.2: Great Sphinx of Giza (Source: https://en.wikipedia.org/wiki/Sphinx)

The long-term durability of ancient mortars and concretes, such as the block making the pyramids has prompted research into the nature of these ancient compositions. Davidovits proved such ancient products are not only physically more durable, but also more resistant to acid attack (Davidovits, 1987).

In 1940, Belgian scientist Purdon discovered that the alkali addition produced a new rapid hardening binder. Thus produced alkali-acivated slag cement was used in large scale construction as early as 1950s. In 1957, Victor Glukhovsky noted that rocks and clay minerals react during alkali treatment to form sodium alumino-silicate hydrates (zeolites), and named the concretes produced with this technology "soil silicate

concretes" and for the binders "soil cement". Since 1960's scientists have been trying to synthesized zeolites and feldspathoids similar to natural integrated silica and alumina.

It was found that ancient concrete contain calcium silicate hydrate (C-S-H) gel, which is also the main part of the Portland cement. Later on Campbell and Folk showed the long term durability of ancient concrete and mortars which contained high levels of zeolitic and amorphous compounds (Campbell and Folk, 1991). Davidovits and his co-workers, called this new class of mineral polymer as alkali-activated aluminosilicate geopolymers or simply geopolymers. The name proposed because of the similarities with organic condensation polymers in regards to their hydrothermal synthesis (Davidovits, 1982; Davidovits and Sawyer, 1985).

The first paper on synthesis of geopolymers was published by Joseph Davidovits and Cordi in 1979 (Davidovits and Cordi, 1979). According to Davidovits geopolymers were invented in search of a heat-resistant, non-flammable and non-combustible 'inorganic polymer' after numerous plastic-related catastrophic fires in France between 1970 and 1973 (Davidovits, 1991 and 1994a). The very first geopolymer was synthesised by mixing kaolinite with ground quartz in cold or hot sodium hydroxide solution (Davidovits and Cordi, 1979). Davidvoits used the simple hydrothermal condition in alkaline medium for the synthesis of mineral feldspathoids and zeolites. The aluminosilicate kaolinite reacts with NaOH at 100-150 °C and polycondenses into hydrated sodalite (a tectoaluminosilicate, a feldspathoid) or hydroxysodalite (Davidovits, 2011).



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; Duxson et al., 2007 and Rahier et al., 1996). The manufacture of OPC not only consumes a significant amount of natural resources and energy but also releases a substantial quantity of greenhouse gases (Davidovits, 1994 and McCaffrey, 2002).

The use of alkali materials and aluminosilicates to form cement is broadly referred to as 'geopolymer technology' also known as alkali-activated cement and inorganic polymer concrete in various parts of the world. Geopolymer technology provides comparable performance to traditional cementitious binders and advantages of the reduction of greenhouse emissions, increasing of fire and chemical resistance and waste utilization. Numerous structures have been constructed in the intervening years though no commercial entities have carried this through to industrial scale. Zeobond staff members have analyzed these structures, now over 50 years old, focusing on their inherent durability (http://www.zeobond.com/geopolymer-history.html).

#### 2.3 Chemistry of Geopolymerisation

A polymer is a substance in which the molecule consists of a large number of low molecular mass base units or monomer that are connected by primary bonds. If A is a monomer molecule then the polymer may be represented by [-A-]<sub>n</sub>, where n is an integer called degree of polymerization. In 1920 Herman Staudinger postulated that those colloidal particles were composed of a single, very long molecule called macromolecule. Polymers can be classified in different ways such as by origin, chain structure, thermal behavior, chain configuration, polymerization mechanism and application (Challa, 1993).

Synthetic organic polymer or simply polymers are the most important class of macromolecular material. Many organic polymers are composed of hydrogen and carbon; their backbones are a string of carbon atoms. Inorganic polymers are made up of monomers containing inorganic elements other than carbon and linked by mainly covalent bonds. The most common inorganic polymers are some natural silicates and synthetic poly(siloxanes).

Hardening (setting) of Geopolymer cement (GP) through polycondensation of Potassium Oligo-(sialate-siloxo) into Potassium Poly(sialate-siloxo) cross linked network.

#### 2.3.1 Mechanism of geopolymer synthesis

Glukhovsky during 1950s proposed a general mechanism for alkali activation of materials comprise of silica and reactive alumina. The Gluhhovsky model divides the process into three stages (Glukhovsky, 1959):

- (a) destruction-coagulation,
- (b) coagulation-condensation and
- (c) condensation-crystallization.

More recently, researchers have elaborated and extended Glukhovsky theories and applied the accumulated knowledge about zeolite synthesis to explain the geopolymerisation process (Duxson et al., 2007; Fernandez-Jimenez and Palomo, 2005; Fernandez-Jimenez et al., 2006; Provis et al., 2005 and van Deventer et al., 2007).

The reaction mechanism shown in the following Figure 2.2 outlines the key processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate. It should be noted that the potential requirement for processing of raw materials by fine grinding, heat treatment etc. to vary the reactivity of aluminum in the system is not for the sake of simplicity. These processes are largely coupled and occur concurrently. Dissolution of the solid aluminosilicate source by alkaline hydrolysis (consuming water) produces aluminate and silicate species (most likely in monomeric form) into solution has always been assumed to be the mechanism responsible for conversion of the solid particles during geopolymerisation. The species released by dissolution are incorporated into the aqueous phase, which may already contain silicate and aluminosilicate species is thereby formed and the speciation equilibria within these solutions have been studied extensively (Swaddle, 1994 and 2001).



Figure 2.3: Conceptual model for geopolymerisation (source: Duxson et al., 2007)

It was proposed that the chemical mechanism takes place in each step of geopolymerisation process and can be summarized into the following five steps (Xu and van Deventer, 2000 and Xu, 2002):

1. *Dissolution reaction:* Dissolution involves the formation of mobile precursors through the complex action of hydroxide ions. Aluminosilicates are dissolved in the alkaline solution to produce Si and Al monomers.

Ai-Si source + MOH  $\rightarrow$  M<sup>+</sup>OSi(OH)<sub>3</sub> + M<sup>+</sup>Al(OH)<sub>4</sub> monomer monomer

- 2. *Diffusion*: Al and Si species diffuse into the gel phase after leached from the surface of the aluminosilicate particle. This reduces the concentration of Al and Si species at the particle surface which enhance further dissolution from the surface.
- 3. *Polymerization*: Polymerization of monomers then takes place to form the highly ordered dimer which further reacts with another monomer or dimer or Si-oligomers to form higher oligomers of varying geometries, i.e. linear, branched or cyclic.

 $^{-}OSi(OH)_{3} + M-OSi(OH)_{3} + M^{+} \rightarrow M-OSi(OH)_{2}-O-Si(OH)_{3} + MOH$ monomer monomer dimer

The activation energy for forming an Al-O-Si linkage is lower than forming a Si-O-Si linkage. Subsequently, the polymerization between Al complex and Si complex will take place in preference to the polymerization between the Si complex (Xu, 2002).

- 4. *Formation of Aluminosilicate gel*: Formation of (-Al-O-Si-) bond network by reacting the M<sup>+</sup> and the higher Si-oligomer.
- 5. *Polycondensation and Hardening Process*: It was believed that the geopolymeric gel was transformed to the final structure either through another dissolution and crystallization or solid-state mechanism. However at this stage of hardening, there is no major movement of particles, but leaching and diffusion between particle surface and the gel phase may still occur and a slight movement of paste in capillary pores may also take place.

All reaction steps are taking place simultaneously; it is difficult to isolate each reaction step for detailed examination.

The mechanism is based on the thought of involvement of major three steps proposed by Davidovits for synthesis of geopolymer from metakaolin MK-750 that takes place in seven steps.

Step 1: Alkalination and formation of tetravalent Al in the side group sialate -Si-O-Al- $(OH)_3$ -Na<sup>+</sup>

The Alkalination takes place in the first step of the mechanism which results in the tetravalent aluminum group formation.

*Step 2*: Alkaline dissolution starts with the attachment of the base OH- to the silicon atom, which is thus able to extend its valence sphere to the penta-covalent state.



The hydroxide then attacks the attached silicon in the second step, taking it to a pentacovalent state and a negatively charged central Si atom. This leads to the cleavage of the second Si as a silanol (Si-OH) group.

*Step 3*: The subsequent course of the reaction can be explained by the cleavage of the siloxane oxygen in Si-O-Si through transfer of the electron from Si to O, formation of intermediate silanol Si-OH on the one hand, and basic siloxo Si-O- on the other hand.



The third step of the mechanism leads eventually to the production of the *ortho*-sialate molecule.

*Step 4*: Further formation of silanol Si-OH groups and isolation of the *ortho*-sialate molecule, the primary unit in geopolymerisation.



The *ortho*-sialate molecule shown as the product in the fourth step of the mechanism is the major subunit of geopolymerisation.

*Step 5*: Reaction of the basic siloxo Si-O- with the sodium cation Na<sup>+</sup> and formation of Si-O-Na terminal bond.



In the fifth step, the cation bonds with the basic siloxo, Si-O-, to form a terminal bond. These steps show the polymerization of these subunits into the larger amorphous units that make up the final structure of the Na-poly(sialate-disiloxo).

*Step 6a*: Condensation between *ortho*-sialate molecules, reactive groups Si-ONa and aluminum hydroxyl OH-Al, with production of NaOH, creation of cyclo-tri-sialate structure, whereby the alkali NaOH is liberated and reacts again and further polycondensation into Na-poly(sialate) nepheline framework.



*Step 6b*: In the presence of waterglass (soluble Na- polysiloxonate) one gets condensation between di-siloxonate  $Q_1$  and *ortho*-sialate molecules, reactive groups Si-ONa, Si-OH and aluminum hydroxyl OH-Al-, creation of *ortho*-sialate-disiloxo cyclic structure, whereby the alkali sodium hydroxide is liberated and reacts again.



In step six, the condensation results in a complex frame work with a cyclo-tri-sialate and *ortho*-sialate-disiloxo structures that does not easily line up in perfectly crystalline rows.

*Step 7*: Further polycondensation into Na-poly(sialate-disiloxo) albite framework with its typical feldspar crankshaft chain structure.



However, the structure in step seven shows the ordered nature of the final geopolymers that give the final product its amorphous to semi-crystalline nature. This mechanism is the same for both the Na and K forms of the poly(sialate-disiloxo) geopolymer structures can be interpreted (www.geopolymer.org/science/about-geopolymerisation/2).

Extensive research has been carried out, but still there are difficulties in analyzing the heterogeneous nature of most of the aluminosilicate sources such as metakaolin, fly ash and the amorphous nature of the resultant product formed.

# 2.3.2 Structure of gopolymer

The chemical composition of a geopolymer material is similar to natural zeolitic materials but its microstructure is amorphous (Davidovits, 2008). The polymerization process involves a substantially fast chemical reaction under alkaline conditions on Si-Al minerals, resulting in three-dimensional polymeric chains and ring structures consisting of Si-O and Al-O bonds (Davidovits, 1994d). It is proposed that the geopolymer gel can diffuse into larger interstitial spaces between the particles (Hua and van Deventer, 2000). A proposed structure of geopolymer is shown in the following Figure 2.4:



Figure 2.4: Proposed geopolymer structure (source: Barbosa, 2000)

The polysialate network is a framework three-dimensional structure of SiO<sub>4</sub> tetrahedral stacking on top of another in all directions with varying degrees of aluminate substitution. The <sup>27</sup>Al MAS-NMR study has revealed that all of the Al<sup>3+</sup> in the polysialate network is in the IV-coordination. Consequently, cations such as Na, K and Ca are required for charge neutralisation on the negatively charged AlO<sub>4</sub> tetrahedral units. The term 'sialate' is an abbreviation for silicon-oxo-aluminate and is used here to describe the bonding of silicon by bridging oxygen. The proposed empirical formula of poly(sialates) is (Mindess et al., 1981):

$$M_p \{(SiO_2)_z AlO_2\}_p .w H_2O$$

where M = Na, K and/or Ca, *p* is the degree of polycondensation, *z* is either 1, 2 or 3 and *w* describes the water content of the composite. The poly(sialate) oligomers are described as chain and ring polymers with Si<sup>4+</sup> and Al<sup>3+</sup> in IV-fold coordination with oxygen and range from amorphous to semi-crystalline. The oligomeric building units are depicted below in the following Figure 2.5:



Figure 2.5: Geopolymer types with aluminosilicate structure (Davidovits, 1991 and 1994a)

The different types are abbreviated PS for poly(sialate), PSS for poly(sialate-siloxo), and PSDS for poly(sialate-disiloxo) (Davitovits, 1994a). The subunits alternate between Si and Al units covalently share oxygen atom in order to make the larger macromolecules called geopolymers. The presence of an alkali metal as a positive ion is necessary to the geopolymer structure because it balances the negatively charged aluminate in IV-fold coordination (Davitovits, 1997).

Silicon is always 4-coordinated, while aluminum ions can be 4 or 6-coordinated in alumino-silicate structure. The co-ordination number of aluminum in the starting materials has an effect on its eventual bonding in the matrix. A highly reactive intermediate gel phase is believed to form by copolymerization of individual aluminoand silicate species. There are quite few studies 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 and Deventer, 2000).

#### 2.4 Synthesis of Geopolymer

Geopolymers are formed by the reaction between an alkaline solution and an aluminosilicate rich source. The product geopolymer has an amorphous 3-dimensional structure similar to that of an aluminosilicate glass. However, unlike a glass, these materials are formed at low temperature and incorporate an aggregate skeleton and a reinforcing system, during the process. Geopolymers can be considered as a member of the family of silicon based inorganic polymers, that can be described by sol-gel silica technology (Hench, 1998), where silicon ions are dissolved from the aluminosilicate source. The polymer chains so produced can be represented by:

In the polymer chain so called geopolymer where some  $Si^{+4}$  ions are replaced by  $Al^{+3}$  ions and are represented as:

The complex member of the family is commonly known as Alkali-Activated Cement. When Ca is introduced into the polymer chain, the resulting geopolymer matrix consists of a mixture of phases represented by - Si - O - Si - O - Al(Ca/Na) - Si - O - Si - and Calcium silicate hydrate (CSH) phases (Gourley, 2014).

Geopolymerisation involves the chemical reaction of aluminosilicate oxides  $(Al^{3+} in IV-V fold coordination)$ , with alkali and calcium polysilicates, yielding polymeric Si-O-Al bonds, for instance (Davidovits, 2002).

$$2(Si_2O_5, Al_2O_2) + K_2(H_3SiO_4)_2 + Ca(H_2SiO_4)_2 \rightarrow (K_2O, CaO)(8SiO_2, 2Al_2O_3, nH_2O)$$

The reactants are an alkali metal hydroxide/silicate solution (chemical activator) and an aluminosilicate source acts as binder. The binder needs to have a significant proportion of the silicon and aluminum ions held in amorphous phases. The aluminosilicate source may be fly ash, ground granulated slags or metakaolinite or any fine aluminosilicate.

The geopolymerisation process involves three separate but inter-related stages. Initial mixing of alkaline solution dissolves silicon and aluminum ions from the amorphous phases of the source. The binder is the primary feedstock but any amorphous phases in

the aggregate skeleton (stone or sand particles) will also react during this stage. During the process, neighboring silicon or aluminium hydroxide molecules then undergo a condensation reaction where adjacent hydroxyl ions from these near neighbors condense to form an oxygen bond linking the molecules. The application of mild heat (typically ambient or up to about 90 °C) causes these "monomers" and other silicon and aluminium hydroxide molecules to poly-condense or polymerize to form rigid chains of oxygen bonded tetrahedral (Gourley, 2014).

The main process difference between ordinary portland cement (OPC) and geopolymer cement is that OPC relies on a high-energy manufacturing process that imparts high potential energy to the material via calcinations, i.e., the activated material reacts readily with a low energy material such as water. On the other hand, geopolymer cement uses very low energy materials, like fly ashes, slags and other industrial wastes and a small amount of high chemical energy materials (alkali hydroxides) to bring about reaction only at the surfaces of particles to act as glue. This approach results in a very large energy saving in the production of geopolymer cement. Geopolymer cements have been proposed as a more eco-friendly alternative as their production does not involve limestone calcinations (Duxson et al., 2007). Alkali-activated aluminosilicate binders are cement-like materials that can be formed by the reaction of calcined clays e.g. metakaolin (Duxson et al., 2007; Wang et al., 2005 and Zhang et al., 2012).

Recently geopolymer concrete brought the attention of many researchers worldwide. The use of industrial by-products such as FA, GGBS, RHA, metakaolin, silica fume, limestone powder, and shale oil ash in the development of geopolymer mortar and the concrete is becoming more common (Sakulich, 2011).

#### Metakaolin based geopolymers

Kaolin clay is normally used for the production of chinaware. However, when it is heated to approximately 800 °C, it becomes activated as metakaolin, it possesses pozzolanic properties. Although it requires heat to produce, metakaolin additions to cement increases its strength substantially (Curcio et al., 1998; De Silva and Glasser, 1992; Potgieter-Vermaak and Potgieter, 2006).

The geopolymerisation of metakaolinite activated by alkali and alkali silicate solutions was extensively studied. From the study it was revealed that the geopolymerisation process of metakaolinite under alkali activation can be occurred in three stages: (I) destruction, (II) polymerization and (III) stabilization shown in the following Figure 2.6:



Figure 2.6: Sketch of the geopolymerisation, including deconstruction, polymerization and stabilization of freshly formed structure (source: Yao et al., 2009)

The alkali concentration of liquid activators, modulus of alkali silicate solutions and reaction temperature had different effects at different stages. The reaction rate increased with the declining of modulus of potassium silicate solution during stages I and II. When the silicate activator modulus was 1.6, the polymerization stage was extended remarkably, which is also consistent with previous report (Provis and van Deventer, 2007a). The study also suggests an optimum reaction temperature could increase the reaction rate and also the extent of reaction of the raw materials (Yao et al., 2009).

A basic conceptual model for geopolymerisation was described and briefly summarized in Figure 2.6. This model was originally applied for the geopolymerisation of metakaolin. The diagram shown in Figure 2.6 indicates the reaction process, the potential combination of polymeric silicate species with aluminate monomers or the direct participation of monomeric species in the later oligomerisation/crystallisation reactions. It was used to understand the influence of various different synthesis parameters on the process of geopolymerisation. For example, a reaction kinetic model using a sequence of reactions based on the process had been shown to provide a quantitatively accurate description of the measured heat evolution during the early stages of the geopolymerisation of metakaolin shown in the following Figure 2.7 (Provis et al., 2005):



Figure 2.7: Schematic outline of the reaction processes involved in geopolymerisation (source: Provis et al., 2005)

The effects of carbonation in alkali silicate-activated slag and slag/metakaolin blends have been studied. From the study it was reported that the carbonation was more rapid in the geopolymer samples containing more metakaolin also high water/binder ratio contributed the rapid carbonation, whereas higher alkalinity in metakaolin-containing systems led to a higher extent of formation of aluminosilicate binder components and thus reduced the carbonation rate (Bernal et al., 2010).

#### Fly ash (FA) based geopolymers

Fly ash is a by-product which is generated during the combustion of coal in thermal power plants, kiln etc. It contains mainly SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> along with CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, MnO, etc. According to the ASTM C618, FA can be classified as being either Class F or

Class C Fly ash with Class C contains higher levels of calcium (Guo et al., 2010). Fly ash with lower levels of calcium was preferred for geopolymers because high amount of calcium can impact the process of polymerization and change the microstructure of the final product (Temuujin, 2009a). Fly ash has become material of interest for geopolymer synthesis due to alumino–silicate composition, low water demand and high workability (Bakharev, 2005; Goretta, 2007; Palomo et al., 1999; Puertas et al., 2000; Skvara et al., 1999; Swanepoel, 2002; van Jaarsveld and van Deventer, 1999).

During geopolymerisation, fly ash react with alkaline medium and specifically aqueous solutions of polysialates leading to the formation of cementitious material, comprising of alumino–silicate–hydrate (A–S–H) gel (Swanepoel, 2002). Fly ash based geopolymers had shown good mechanical strength and enhanced durability (Goretta, 2007; Fernandez-Jimenez and Palomo, 2005; Swanepoel, 2002; van Jaarsveld and van Deventer, 1999).

A fly ash-based geopolymer was synthesised by activating Class F fly ash with an alkaline activator (waterglass and NaOH solution) at a constant liquid/solid mixing ratio. Increasing the waterglass content in the activator significantly increased in the geopolymerisation reaction rate and the strength of geopolymer was reported. Both the total Si and water contents played important roles in geopolymerisation reactions (Bakri et al., 2011).

Strength development of geopolymer synthesized from fly ash with and without addition of crystalline phases was dependent on type of the additive materials. Quartz-added geopolymers displayed higher compressive strength values than that of corundum-added geopolymers due to a better reactivity shown by quartz crystalline phase. A Compressive strength of 65 MPa was achieved by starting materials with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> more than 3.5 which obtained by quartz additions. However addition of corundum crystalline phase had shown lower reactivity and the strength of geopolymers achieved about 33 MPa. It was found that the crystalline phase did involve in the geopolymerisation process in some degree (Atmaja et al., 2011).

Geopolymer synthesized from the fly ash obtained from coal fired thermal power plant, and granulated blast furnace slag (from integrated cement plant, Chattisgarh, India) showed a maximum compressive strength of 45 MPa. The reaction kinetics of fly ash based geopolymer was studied by isothermal conduction calorimeter. The influence of granulated blast furnace slag (GBFS) on reactivity of fly ash geopolymer was studied at room temperature as well as at elevated temperature. It was observed that at room temperature (27 °C) geopolymer reaction was dominated by GBFS activation by formation of CSH which improved the setting time and compressive strength, whereas at 60 °C due to combined interaction of fly ash and GBFS were found (Kumar et al., 2010). In another study through mechanical activation of fly ash, the development of high strength geopolymeric material with compact microstructure was achieved (Kumar et al., 2005).

Curing temperature is one of the important factors for geopolymerisation. The temperature, curing period and relative humidity are the curing conditions impacts the creation of microstructures and also affect the mechanical characteristics of alkaline-activated fly ash (Komljenovic et al., 2010). The gopolymer sample cured at 65 °C had a maximum compressive strength of about 33 MPa after only 4 days of curing period. However, further increase in curing period beyond 4 days produces less compressive strength. The curing period more than 8 days resulted in a short decrease of compressive strength. Also, the compressive strength of geopolymer samples gradually decreased when cured at temperatures higher than 65 °C.

A study has shown that the compressive strength of fly ash based geopolymers did not develop significantly when cured at temperatures in excess of 60 °C and a recommendation was made that fly ash based geopolymers should be cured at 65 °C (Hardjito and Rangan., 2005). Another study had shown that the curing temperature accelerates the reaction in fly ash-based geopolymers (Palomo et al., 1999). The curing temperatures between 40 and 80 °C for 4 to 48 hours were found to have one of the important conditions for the synthesis of geopolymer (Temuujin et al., 2009).

The compressive strength of specimens heat-cured for less than 4 days at temperatures below 80 °C was higher than those cured at ambient temperatures (Xu et al., 2010). A study claimed that longer and hotter curing times would lead to weaker geopolymer

structures due to the negative effect on the geopolymer structures (van Jaarsveld et al., 2002).

An investigation was made regarding the effects of aggregate content, alkaline solution to FA ratio (A/FA), sodium silicate to sodium hydroxide ratio, and curing method on FA based geopolymer concrete. Geopolymer concrete thus produced from FA had a compressive strength of 55 MPa at 28-days. The specimens had higher tensile and flexural strength, less expansion and drying shrinkage than the OPC control mix (Olivia and Nikraz, 2012).

#### Slag based geopolymers

Granulated blast furnace slag (GBFS) is a by-product of the steel production industries. It is a glassy, granular material essentially consisting of SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub> and MgO. It is formed when molten blast furnace (BF) slag produced as a byproduct in iron making is rapidly cooled, usually by immersion in water and then ground to improve its reactivity.

In the alkali activation of GBFS, the main reaction product was a hydrated calciumsilicate (C–S–H) gel with low C/S ratio. The C–S–H gel improves the setting and strength characteristic of geopolymer (Buchwald et al., 2005, 2007 and Yip et al., 2003, 2004). Contrary to fly ash, it is a latent hydraulic binder that can develop strength due to the formation of cement-like compounds as a result of its composition that contain compounds similar to those found in cement clinker. It can be further activated with alkali activators, especially calcium hydroxide. GGBFS is usually milled to a finer composition than OPC (Maeng, 1996), and as such it can have several beneficial effects if added to cement or concrete mixtures. Just like fly ash, it can form an ingredient in the raw mix for CSA cements, AACs and geopolymers (Komnitsas and Zaharaki, 2007 and Mozgwa and Deja, 2009).

The compressive strength value of 10 MPa in case of geopolymer from fly ash which were found increased with the increase in GBFS content. The maximum compressive strength 45 MPa was reported when 50 percent of ground granulated blast furnace slag (GBFS) was added. These improvements were noticed due to improvement in setting time and formation of cementitious calcium silicate hydrate gel (Kumar et al., 2010).

Replacements of conventional aggregate in concrete using the waste product of steel industry like steel slag, ground granulated blast furnace slag, and fly ash has been extensively studied. It was found that, the compressive strength of concrete increases upto 40%, when 75% of fine aggregate and coarse aggregates both are replaced by steel slag (Pajgade and Thakur, 2013).

# Zeolite based geopolymers

Geopolymers from mechanochemically treated clinoptilolite were synthesized using sodium hydroxide and sodium silicate solutions had shown increasing compressive strength up to around 25 MPa with increasing curing time (Jha and Hayashi, 2009).

A study was made to evaluate the dependence of activator ratio, curing time and curing temperature on the mechanical strength of geopolymers synthesized from natural zeolite. The results showed that the increase in the activator ratio as well as that of curing time favored mechanical strength of the geopolymer. This indicates that the use of activator on non commercial zeolite could be use in the synthesis of geopolymers (Villa and Gomez, 2010).

A study on zeolite-geopolymer hybrid materials was conducted using kaolin as a starting material. The relationship between the properties of initial kaolinitic clays, their metakaolin, and the final zeolite-geopolymer hybrid bulk material products was investigated. It was found that increase in specific surface area of metakaolin increases the amount of zeolite formed in the final products. Due to higher specific surface area, the solubility of the Al and Si ions increases resulting in an increase in zeolite formation. However, in the study the compressive strength of the zeolite-geopolymer hybrid materials and the amount of zeolite was not very clear (Takeda, 2013).

#### 2.5 **Properties of Geopolymer**

The traditional use of construction materials such as bricks, solid blocks, hollow blocks, pavement blocks, concrete and tiles are being produced from the existing natural resources. This causes damaging the environment due to the continuous exploration and depletion of natural resources. Imparting various toxic substances such as carbon monoxide, carbon dioxide, oxides of nitrogen, oxides of sulfur, and suspended particulate matters are invariably emitted to the atmosphere during the process of production of construction materials. This severely affects human health as well as their living standard. Therefore, the issues related to environmental conservation have a great importance in our society in recent years (Xue et al., 2009).

The cost of construction materials is increasing because of high demand, scarcity of raw materials, and high price of energy. Therefore, energy saving and conservation of natural resources, the use of alternative constituents in construction materials is now became a global concern. 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).

Geopolymers are hard, sulphate and corrosion resistant have low shrinkage and able to withstand high temperatures. The fire resistance of geopolymer has been verified to be well in excess of double that of traditional concrete (http://www.zeobond.com/geopolymer-history.html).

Geopolymer cement based on alkali-activated fly ash has been found to exhibit a high density of pores in the micrometer size range (Palomo et al., 1999). The presence of pores in the matrix of geopolymers was intrinsic, independent of the starting materials and the processing routes while the density of pores was influenced by the ratio of starting materials. These polymers exhibited properties similar to many non-metallic materials including formability comparable to epoxies, high temperature stability, chemical resistance comparable to ceramic oxides and compressive strengths superior to concrete (Hos et al., 2002) and had potential for civil engineering applications such as pavement blocks, precast concrete blocks, retaining walls (Rapazote et al., 2011).

The performance of geopoymer is comparable to Ordinary Portland Cement in several applications, also it has additional advantages, abundant raw material resources, simple production method, rapid development of mechanical strength, no/low alkali-silica reaction (ASR), excellent durability, high fire resistance, superior resistance to chemical attack and able to immobilize toxic and hazardous wastes. These characteristics properties have made geopolymer great interest of research as 'an ideal material for sustainable development' (Ahmari and Zhang, 2012; Davidovits, 1994a, 1988 and 1991; Duxson et al., 2007; Lyon et al., 1996; Majidi et al., 2009; Xu, 2002; Zhang et al., 2011 and Zongjin et al. 2004). 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 (Jaarsveld et al., 1996). The geopolymer material can be used in various applications, such as fire and heat resistant fibre composites, sealants, concretes, ceramics, etc., depending on the chemical composition of the source materials and the activators. There is large potential for geopolymer concrete applications for bridges, such as precast structural elements and decks as well as structural retrofits using geopolymer-fiber composites. Other potential near term applications are precast pavers and slabs for paving, bricks and precast pipes (Aleem and Arumairaj, 2012).

#### 2.6 Applications of Geopolymer

The physical properties of the hardened geopolymer are influenced by the Si/Al ratio of the geopolymer network. Below a Si/Al ratio of 3:1, the resultant 3D nets are rigid, suitable as a concrete, cement or waste encapsulating medium. As the Si/Al ratio increases above 3, the resultant geopolymer becomes less rigid and more flexible or "polymer-like" (Davidovits, 1991 and 1999). The following Table 2.1 summarizes the successful applications carried out since 1979 with geopolymers of different types (Davidovits, 2002). With higher Si/Al ratios, up to 35:1, the resultant crosslinked 2D chains are more suited as an adhesive or sealant, or as an impregnating resin. Such high Si/Al ratio geopolymers form resins with low viscosity, sufficient to wet out reinforcing fibres, strands or mats, producing laminates with flexural strengths in excess of 650 MPa (Hammell, 2000).

Si:Al ratio	Polymeric	Applications		
	character	Low	High	
		technology	Technology	
Si:Al=1:1		- Tiles		
		- Ceramics		
	3D	- Fire protection		
Si:Al=2:1	Network	- Cements		
		- Concretes		
		- Radioactive and toxic		
		Wastes management		
Si:Al=3:1		- Foundry equipment	- Tooling for aeronautics	
		- Fire resistant fiber glass	- Heat resistant composites	
	2D	Composites		
Si:Al>3:1	Crosslink	- Sealants for industry	- Tooling for aeronautics	
20:1 <si:al< td=""><td></td><td></td><td>- Fire and heat resistant</td></si:al<>			- Fire and heat resistant	
and			fiber composites	
Si:Al>35:1				

 Table 2.1: The applications of the various geopolymeric binders and Si/Al ratio dependence (http://www.geopolymer.org)

In recent years, the alkali activated inorganic cementitious compositions have reached its production on commercial scale and marked by American cement manufacturer Lone Star Industries, Inc. under the brand name PYRAMENT<sup>®</sup> blended cement which was produced from the development carried out on inorganic alumino-silicate polymers called geopolymer (Davidovits, 1991, 1994a and 1994b; Palomo et al., 1999). Such geopolymer cements are acid-resistant cementitious materials with zeolitic properties, developed for the long-term containment of hazardous and toxic wastes (USA Patent No. 4, 6:349-386 and Davidovits, 2002).

Since 1986, the French aeronautic company Dassault Aviation has been using geopolymer mold and tooling in the development of the Rafale fighter plane (Davidovits, 2002). In Australia, on September 28, 2014, the newly completed Brisbane West Wellcamp airport becomes the greenest airport in the world. More than 30,000 cubic meters, cement-free geopolymer concrete was used to save more than 6,600 tones of

carbon emissions in the construction of the airport. The University of Queensland's Global Change Institute (GCI) is the world's first building to successfully use geopolymer concrete for structural purposes (www.geopolymer.org).



Figure 2.8: (a) Brisbane west wellcamp airport, Australia (b) Queensland's University GCI building made from structural geopolymer concrete. (Source: www.geopolymer.org)

Chromatography is a widely used technique for separating mixtures of organic compounds by passing them in solution through a column packed with a solid stationary phase. The efficiency of the separation depends on a number of factors, including the chemical binding of the various components to the stationary phase and the morphology of the stationary phase particles, which determines the flow of the solvent through the column. Inorganic polymers have been shown to provide a cost-effective, readily synthesized and efficient alternative for both silica and alumina chromatography stationary phases (Alzeer et al., 2013 and MacKenzie, 2015).

Luminescent materials find a number of present-day applications in television and computer monitor screens, oscilloscopes and radar screens, electron microscope screens and LEDs for general lighting and specialized applications. The interesting prospect of synthesizing geopolymers with luminescence properties tailored into the structure has been investigated (Rogers and MacKenzie, 2014). These interesting properties of geopolymers led to continue the development of materials with new functionalities designed into their structure, or as scaffolds for other Compounds (MacKenzie, 2015).

# CHAPTER 3 EXPERIMENTALS

# 3.1 Materials and Methods

# 3.1.1 Selection of raw materials

The coal fly ash (CFA) was obtained from Uma-Maheshwor Brick Factory of Kirtipur, Kathmandu. Demolished-cement-sand-mixture (DCSM) waste was selected from demolition area near Nayabazar, Kirtipur, Kathmandu (brick and gravel was not included). Demolished cement sand-concrete mixture (DCSCM) was obtained from demolished part of Central Library, Tribhuvan University, Kirtipur, Kathmandu. Brick blocks (BD-K) were obtained from demolition area of Kirtipur, Kathmandu. Brick blocks (BD-J) were taken from the demolished garbage site of National Metallurgical Laboratory, Agrico, Jamshedpur India.

All raw materials were ground manually and separately by using *Khal*, mortar-pestle to obtain in fine powder form. The powder was further modified with 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, UK) at 80 °C for overnight.

# **3.1.2** Fabrication of milling machine

A new table fan was purchased and was dismantled; the motor of the fan was connected to crossed strip of iron to which four plastic bottles were fixed by means of strip of tin. The regulator of the fan was also assembled in order for controlling the speed of thus assembled milling machine. It was then taken to carpenter to give its final shape.

The plastic bottle was filled with 2 mm diameter iron ball (25 g), construction waste (5 g) (which was first ground manually by using *Khal*, mortar-pestle to obtain in fine powder form) and distilled water (60 mL) and then milling was started through its power supply and regulated for 15 - 30 minutes. The pictorial view of above set up is shown in the following Figure 3.1:



**Figure 3.1:** (a) Dismantled fan motor (b) Motor connected with crossed iron strip to which four tin sample holders are connected (c) Holders containing plastic bottle filled with distilled water placed for rotation and (d) Self-assembled milling machine.

# 3.1.3 Use of activator solutions

Laboratory grade pellet of NaOH (97%, Merck, Germany), Potassium hydroxide (85%, SD Fine-Chem. limited, India), sodium silicate pentahydrate (97%, SD Fine-Chem. limited, India), liquid sodium silicate solution ( $\geq$  10% NaOH,  $\geq$  27% SiO<sub>2</sub>, Sigma-Aldrich, Germany), liquid sodium silicate (Na<sub>2</sub>O: 9.02 %, SiO<sub>2</sub>: 25.8 % and H<sub>2</sub>O: 65.18 %, Lobe Chemme, India) were used to prepare the geopolymer products CFA, DCSM, BD-K1, BD-K3, SCM and BDSCM; DCSCM and BD-K2; A-2, B-2, BDAM, BDMK and BDL respectively.

#### 3.2 Variation of Several Parameters

#### 3.2.1 Alkali concentration

The dried coal fly ash powder 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 (2.6 cm  $\times$  2.6 cm  $\times$  1.0 cm), air bubbles were removed with the help of ultra sonicator (Branson 2510E-MTH, USA) sealed with thin plastic films and allowed to cure for 4 days in oven at 40 °C.

Demolished cement sand mixture (DCSM) waste was blended manually for 2 minutes with various concentrations of sodium hydroxide solution (2 to 8 M) separately using mortar and pestle. This mixture was then transferred to plastic mould (length  $\times$  breadth  $\times$  height: 2 cm  $\times$  2 cm  $\times$  2 cm cubic) and was sealed to prevent water loss. Care was taken to avoid air bubbles. The mould was then placed in oven for curing at 40 °C for 6 days.

DCSCM powder was 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 at 40 °C for 7 days.

Brick dust (BD-K) was treated with sodium hydroxide solution of 2, 4, 6 and 8 M and were prepared separately to synthesize geopolymer sample BD-K1. The mixture was then transferred to plastic mould ( $2 \text{ cm} \times 2 \text{ cm} \times 2 \text{ cm}$  cubic) and was sealed to prevent water loss. Care was taken to avoid air bubbles. The mould was then placed in oven for curing at 40 °C for 6 days.

For the geopolymer sample BD-K2, brick dust was mixed with sodium hydroxide solution of 2, 4, 6 and 8 M. It was then blended manually for 2 min and casted in a cuboidal mould ( $2.5 \text{ cm} \times 2.5 \text{ cm} \times 2.5 \text{ cm}$ ) at temperature  $12\pm2$  °C and relative humidity of 65.5%. The moulds were then kept in oven at temperature 40 °C for 4 hour and then kept at room temperature.

For the geopolymer sample BD-K3 and SCM, brick dust and sand cement waste dust with sodium hydroxide solution of 2, 4, 5, 6, 7 and 8 M. It was then blended manually for 2 min and separately kept in cuboidal mould (2.5 cm  $\times$  2.5 cm  $\times$  2.5 cm). The mixtures were then cured at 40 °C.

#### 3.2.2 Particle size

The demolished cement sand mixture (DCSM), demolished cement sand concrete mixture (DCSM) and brick dust (BD) were ground and sieved in various sizes as  $\leq$ 53,  $\leq$ 75,  $\leq$ 90 and  $\leq$ 120 µm separately.

These raw materials dust were separately blended manually with the selected 6 M NaOH for 2 minutes and were kept in cuboidal mould. These samples were cured separately for 6 days (DCSM), 7 days (DCSM), 10 days (BD-K1), 7 days (BD-K2), 7 days (BD-K3) 7 days and 7 days (SCM).

#### 3.2.3 Sodium silicate ratio

After the selection of KOH concentration, the mass ratio of  $Na_2SiO_3/CFA$  were varied from 0.25 - 2.00 along with the selected KOH concentration of 7 M. The blended mixtures were then separately placed in cuboidal plastic moulds and allowed to cure for 4 days in oven at 40°C.

Then the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/DCSM (53  $\mu$ m) were varied from 0.5 - 2.0. The mixture was thoroughly mixed with the selected 6N NaOH and particle size of 53  $\mu$ m poured into plastic mould and was cured for 21 days at 40 °C. Finally the curing time was varied in oven at 40 °C.

Further  $Na_2SiO_3/DCSCM$  (53 µm) ratio in between 0.50 - 2.00 was varied and the concentration of NaOH solution was fixed to 6 M. The blended mixtures were placed separately in cuboidal plastic moulds, sealed with thin plastic films and dried in oven for 28 days at 40 °C.

The variations of the mass ratios of sodium silicate (power) to BD-K (53  $\mu$ m) for the geopolymer product BD-K1were varied from 0.5 - 2.0. The mixtures was thoroughly mixed with 6 M sodium hydroxide solution for 2 minutes and transferred to plastic mould and were cured at 40 °C for 10 days.

For the preparation of geopolymer BD-K2, the activator solution was prepared by mixing 1:1 solution (v/v) of 6 M NaOH and liquid silicate and for the geopolymers BD-K3, SCM and BDSCM, the activator solution was prepared by dissolving sodium silicate pentahydrate in 6 M NaOH solution using magnetic stirrer for one hour at  $65-70 \,^{\circ}$ C.

For the synthesis of the geopolymer products A-2 and B-2, the activator solution was prepared by mixing 1:2 solutions of 6 M NaOH and liquid sodium silicate solution.

For the synthesis of the geopolymer products BDAM, BDMK and BDL, the activator solution was prepared by mixing 1:1 solution of 6 M sodium hydroxide and liquid sodium silicate solution. 6 M NaOH was prepared by dissolving NaOH pellet in water before the preparation of activator solution and was kept in closed plastic container to

avoid carbonation. Thus prepared sodium hydroxide was then mixed with liquid sodium silicate solution and was allowed to cool at room temperature for the synthesis of geopolymer. The parameters were held constant in the activator solution was  $SiO_2/Na_2O = 1.16$ ,  $M_2O/Al_2O_3 = 0.88$  in the mixture, water/solid = 0.18 and the sodium hydroxide concentration = 6.0 M. These parameters had shown good mechanical properties according to previous report (Khater, 2012; Khale and Chaudhary, 2007).

# 3.2.4 Dolomite amount

Brick dust (BD-K) and sand cement waste were mixed with 10, 20, 30, 40 and 50 % dolomite waste and were separately blended with the activator solution to prepare the geopolymer products BD-K3 and SCM.

# 3.2.5 Mixture of BD and SCM

The mixture of brick dust (BD-K) and sand cement waste in ratio of 60:40 was mixed with 30 % of the dolomite and was blended with the activator solution. In general, with the increase of brick percentage, the compressive strength of the geopolymeric product also increased (Allahverdi and Najafi Kani, 2009). At the site of collection of construction and demolition waste brick dust and the sand cement dust are in the ratio of approximately 60:40.

#### 3.2.6 Curing time

Finally curing time for the geopolymer product CFA, DCSM, DCSCM, BD-K1, BD-K2, BD-K3, SCM, BDSCM, A-2, B-2, BDAM BDMK and BDL were varied from 6 - 28 days. In addition to that for the sample DCSCM, BDAM and BDL, the compressive strength measurement at 3 days were also performed.

# 3.2.7 Curing temperature

After the selection of alkali concentration, particle size and amount of sodium silicate, in case of the geopolymer sample BD-K2, in addition to curing time, curing temperature was also varied for 40, 50, 60 and 70 °C for 4 hours followed by curing at room

temperature at  $12\pm3$  °C for 7-28 days (during the winter season the room temperature was in the range of at  $12\pm3$  °C).

# 3.2.8 Milling time

The waste brick (BD-J) was divided into small pieces by means of hammer, pulverized and then ball-milled (available at NML, Jamshedpur India) for half an hour (A), one hour (B), one and half hour (C) and two hour (D). The Pulveriser and Ball Mill are shown in the following Figures 3.2 (a) and (b) respectively:



Figure 3.2: (a) Pulveriser (b) Ball-Mill

# 3.2.9 Use of metakaolin and lime

The mixture design for the synthesis of geopolymer is shown in the following Table 3.1:

BD	Lime	Metakaolin	NaOH	Water glass	Water
100	-	-	3.56	20.16	18.22
96	4	-	3.56	20.16	18.22
90	-	10	3.56	20.16	18.22
100	-	-	2.37	26.87	20.42
100	-	-	2.37	26.87	20.42
	BD 100 96 90 100 100	BD     Lime       100     -       96     4       90     -       100     -       100     -	BD         Lime         Metakaolin           100         -         -           96         4         -           90         -         100           100         -         -           100         -         -	BDLimeMetakaolinNaOH1003.56964-3.5690-103.561002.371002.37	BDLimeMetakaolinNaOHWater glass1003.5620.16964-3.5620.1690-103.5620.16100-2.3726.871002.3726.87

 Table 3.1: Mixture designs by weight (in gram) for the synthesis of geopolymer.

Brick dust (BD-J), sodium hydroxide, liquid sodium silicate, water together with the addition of Ca(OH)<sub>2</sub> and metakaolin were used to prepare the geopolymer samples A-2, B-2, BDAM, BDMK and BDL.

Powder brick, metakaolin and lime were dry mixed separately and then the mixed powder was blended with the activator solution. It was mixed for 3.5 minute using DIGI Mortar Mixer, Aimil available at National Metallurgical Laboratory, Jamshedpur India shown in the following Figure 3.3:

The sample were then casted in 5 cm  $\times$  5 cm  $\times$  5 cm steel moulds shown in the following Figure 3.4 at room temperature (32±3 °C) for four hour. The moulds were immediately allowed to tap for 1 minute on the flow table to remove air bubble available at NML, Jamshedpur India shown in the following Figure 3.5:

Samples along with the steel mould were then cured at 60 °C for 24 hour, cooled and then the samples were demoulded and kept in a closed water tank to maintain humidity °C). room temperature  $(32\pm3)$ at The geopolymer was subjected for drying 60 °C for 24 hour before the treatment at measurement of compressive strength so as to improve the mechanical properties (Khater, 2012).



Figure 3.3: Digi mortar mixture



Figure 3.4: Samples casted in steel moulds



Figure 3.5: Flow table

The compressive strength of geopolymer products were measured for 7 - 28 days on an Automatic Compression Testing Machine (Aimil comptest 2000, India).

#### 3.3 Characterization Techniques

#### 3.3.1 X-ray diffraction patterns

The X- ray diffraction (XRD) pattern of the raw samples and fragment from the crushing

tests of few characteristic samples were obtained by a scanning rate of 2 and 1.5 degree per minute and the samples were scanned from 10 to 80° (20). Powder XRD patterns were recorded on X-ray diffractometer using CuK<sub> $\alpha$ </sub> radiation (Bruker D8 Advance Diffractometer, Germany shown in Figure 3.6 available at Central Department of Geology, Tribhuvan University, Kirtipur, National Academy of Science and Technology (NAST), Khumaltar, Kathmandu and at National Metallurgical Laboratory (NML), Jamshedpur, India.

#### **3.3.2** Particle size analysis

The particle size analysis of the raw material in powder form milled for different time interval (30 -120 minute) was carried out by laser particle size analyzer shown in the following Figure 3.7 available at National Metallurgical Laboratory (NML), Jamshedpur, India.



**Figure 3.6:** Bruker, D8 Advance Diffractometer



**Figure 3.7:** Mastersizer S. Malvern, analyzer (Ver. 2.19, Malvern, UK)

#### 3.3.3 Isothermal conduction calorimetric (ICC) analysis

Isothermal conduction calorimeter was carried out at ambient temperature to monitor the geopolymerisation of brick powder and its composition with 4% lime and 10 % metakaolin. The rate of heat evolution during the reaction, dq/dT, at 27 °C was measured for 20 hours using an eight channel isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden) shown in Figure 3.8 available at NML Jamshedpur India. The operation includes the following steps:

- Preparation of alkaline activator solution by dissolving equal volume of 6 M sodium hydroxide and sodium silicate solution.
- (ii) Mixing 7 g of powder sample in the ampoule with 4 mL of alkaline activated solution and
- (iii) Loading of each sample into channels of the calorimeter at an interval of about 60-90 seconds.



**Figure 3.8:** (a) TA AIR, Thermometric AB, Sweden, (b) Eight channel in the calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden).

# 3.3.4 Fourier Transform Infra Red Spectroscopic (FTIR) Analysis

Fourier transform infrared spectroscopy (Nicolet 5700 spectrometer, Thermo Electron

Corporation, USA) was used in this study which was available at National Metallurgical Laboratory, Jamshedpur India and at Department of Chemistry, Indian Institute of Technology, Roorkee.

The sample FTIR analyses were prepared by mixing with KBr.



Figure 3.9: Nicolet 5700 FTIR spectroscopy

# 3.3.5 Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) Analysis

Morphological characterization of the fractured samples was done by a scanning electron microscope (SEM 840, JEOL with a Kevex EDX attachment) which was available at National Metallurgical Laboratory, Jamshedpur India.

# 3.4 Study of Mechanical Properties

#### **3.4.1** Compressive strength measurement

#### **3.4.1.1** Maruto testing machine

For compressive strength measurement, the sample was removed from the plastic mould and polished in various sized sand papers (from 400-800 sizes) to get its smooth surface. The area of the solid smooth sample was measured using Vernier caliper, then the compressive strength of the prepared geopolymers was measured using *MARUTO testing machine* (s56A, Japan) available at National Academy of Science and Technology (NAST), Khumaltar, Lalitpur. Each data of the compressive strength presented in this thesis is the average of three consecutive measurements.

#### 3.4.1.2 Aimil comptest 2000

The compressive strength of the geopolymer products (BDAM, BDMK, BDL, A-2, B-2)

were measured using Compression Testing Machine (Aimil Comptest 2000, India) using the loading rate of 5 KN per second shown in Figure 3.9 available at NML, Jamshedpur India.



Figure 3.10: (a) Aimil comptest 2000, India, (b) Sample failure in the comptest
### 3.4.1.3 SLF 9 load frame machine

The compressive strength of the geopolymer products (BD-K1, BD-K2, BD-K3, DCSM, DCSCM, SCM, BDSCM) were measured using *SLF Load machine* is shown in the following Figure 3.10 available at Central Material Testing Laboratory, Institute of Engineering Pulchowk Campus, Tribhuvan University. The sample was crushed by applying load and was noted. Each data of the compressive strength presented in this thesis is the average of three consecutive measurements.



Figure 3.11: SLF 9 Load Frame Machine.

### 3.4.2 Flexural strength measurement

The flexural strength of the geopolymer products BDAM, BDMK and BDL were measured using *Riehle testing machine* shown in the Figure 3.11 available at NML, Jamshedpur, India. The area of the geopolymer products were measured using Vernier caliper, before the measurement of flexural strength. Each data of the flexural strength presented in this thesis is the average of three consecutive measurements.



Figure 3.12: Riehle testing machine

## 3.5 Study of Physical Properties

Water absorption, apparent porosity and bulk density were determined as per ASTM C373-88 (ASTM, 2006), the geopolymer was first dried in oven at 150 °C for 2 hour and was allowed to cool and dry weight of the geopolymer was taken using triple beam balance. The geopolymer was then boiled for 5 hour in a water bath and allowed to soak for additional 24 hour. The suspended and soaked weights of the geopolymer were taken using a wire loop that was suspended from one arm of the balance.

CHAPTER 4 RESULTS AND DISCUSSION This chapter presents experimental results which represents the average of three consecutive measurements of geopolymers synthesized from coal fly ash (CFA), demolished-cement-sand-mixture (DCSM), demolished-cement-sand-concrete mixture (DCSCM), brick from Kathmandu (BD-K), brick and sand cement waste with dolomite variation and their mixture (BD-K and SCW) and brick from Jamshedpur (BD-J).

## 4.1 Coal Fly Ash Based Geopolymer

### 4.1.1 Characterization of raw CFA and its geopolymer products

The X-ray diffraction pattern of CFA and its geopolymeric products is shown in the following Figure 4.1:



Figure 4.1: XRD patterns of coal fly ash and its geopolymer products.

The XRD patterns of the raw coal fly ash (CFA) have shown the presence of sharp peaks centered at 26.6 ° of 20 angle due to the presence of quartz and/or mullite phase and peak at 20.96 ° and 50.16 ° of 20 angle due to the presence of mullite phase. It occurs normally at high temperature and CFA is the byproduct of the firing of coal much more than 1000 °C. Thus there was the presence of mullite phase in the raw CFA. Only some parts of the quartz crystals which were present in raw material were converted to amorphous during the dissolution process. Thus the quartz peaks are remained in the final products also.

The quartz/mullite phase gets diminishes due to the dissolution of solid aluminosilicate in alkaline medium which is the suitable condition for the nucleation of zeolite phase which can be seen in the XRD pattern of the products. But as the treatment was done in most of the cases at ambient temperature (40 °C), 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 not enhanced further. Also some parts of the mullite phase transform into glassy and semicrystalline phases (Gonzalez et al., 2003 and Lukman, 2011). Also formation of gel phase at fly ash surface that grows outward in alkaline system (Lloyd et al., 2009).

### 4.1.2 Mechanical properties CFA based geopolymer

Compressive strength is a measure of a material's ability to withstand compressive forces, it is point at which the material fails/crushes or the material breaks down.

Compressive strength = 
$$\frac{Force}{Area}$$

The compressive strength is a measure of force per unit area and expressed as one Newton per square millimeter or pounds-force per square inch (psi)

$$1 \text{ MPa} = 1 \text{ Newton/(millimeter)}^2 = 145.0377 \text{ psi}$$

### 4.1.2.1 Variation of alkali concentration

The geopolymer was prepared from coal fly ash (CFA) of particle size  $\leq$ 75 µm and alkali concentrations (KOH) was varied between 3 - 8 M. The compressive strength values of coal fly ash based geopolymer were 0.50, 0.82, 1.16, 1.65, 6.62, 3.95 and 0.66 MPa for the KOH concentration equal to 3.0, 4.0, 5.0, 6.0, 7.0, 7.5 and 8.0 M respectively with 4 days of curing at 40 °C.

The compressive strength of geopolymeric products with the variation of alkali concentration is shown in the following Figure 4.2:



Figure 4.2: Plot of compressive strength of CFA based geopolymer products as a function of KOH concentration.

The increase in the compressive strength with increasing KOH concentration was due to the fact that higher amount of hydroxide ions (OH<sup>-</sup>) facilitate the dissolution of silicate and aluminate species and thus promotes polymerization (Davidovits and Orlinski, 1988; Komnitsas and Zaharaki, 2007 and Yip et al., 2005). 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 (Singh et al., 2005 and Tuladhar 2010). Further, the excess KOH forms potassium carbonate by atmospheric carbon (Barbosa et al., 1999).

The maximum compressive strength of CFA based geopolymer was found at 7 M of KOH and thus this concentration of KOH solution was selected for further study. Use of NaOH instead of KOH, similar trends of results was observed. As sodium hydroxide is more economic than potassium hydroxide, thus sodium hydroxide was selected for further study as an activator.

### 4.1.2.2 Variation of Na<sub>2</sub>SiO<sub>3</sub> to CFA mass ratio

After the selection of potassium hydroxide concentration (7 M), the mass ratio of  $Na_2SiO_3/CFA$  between 0.25 - 2.00 were varied. The compressive strength of geopolymeric products cured at 40 °C is shown in the following Figure 4.3:



Figure 4.3: Plot of compressive strength of geopolymer products as a function of Na<sub>2</sub>SiO<sub>3</sub>/CFA mass ratio.

The compressive strength values of CFA based geopolymer were 8.51, 12.58, 16.79, 20.31, 23.78, 27.20, 28.07 and 26.69 MPa for the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/CFA equal to 0.25, 0.5, 0.75, 1.00, 1.25, 1.50, 1.75 and 2.0 respectively with 4 days of curing at 40 °C.

The addition of Na<sub>2</sub>SiO<sub>3</sub> plays a significant role on the compressive strength of the geopolymer products. Sodium silicate contains self-polymerizing species such as monomer, dimer and larger oligomer containing Si-O-Si chain which influence soluble alumino-silicate units to polymerize (McCormick et al., 1989 and Wang et al., 2005). Also at higher concentration of silicates, the stronger ion pair formation is expected which results in the formation of longer chain silicate oligomer as well as Al–O–Si complexes (McCormick et al., 1989). Thus added silica acts as a binder shown in the reaction below and schematized as (Davidovits, 1991 and 1994c):

$$n(Si_{2}O_{5} Al_{2}O_{2}) + 2n(SiO_{2}) + 4nH_{2}O \xrightarrow{NaOH/KOH} n(OH)_{3}-Si-O-Al^{-}O-Si-(OH)_{3} \dots (1)$$

$$(Ortho(sial ate-siloxo))$$

$$OH \qquad (Ortho(sial ate-siloxo))$$

$$OH \qquad (Ortho(sial ate-siloxo))$$

$$OH \qquad (NaOH)_{3}-Si-O-Al^{-}O-Si-(OH)_{3} \xrightarrow{NaOH/KOH} (Na^{+}/K^{+})-(Si-O-Al^{-}O-Si-O)_{n} + 4nH_{2}O \dots (2)$$

$$OH \qquad (Na/K)-poly(sial ate-siloxo)$$

In the above Equation (1) addition of  $SiO_2$  into  $(SiO_5Al_2O_2)$  in the presence of alkali, forms IV fold co-ordination of Al instead of conventional alumino-silicate oxides, further it forms the final backbone of the geopolymer and charge balance in the matrix shown in Equation (2).

But the large excess silica decreases the rate of geopolymerisation and solidification of the paste takes place prior to completion of reaction (Provis and van Deventer, 2007a and 2007b). Also the excess silicate hinders water evaporation and structure formation (Chang and Chiu, 2003). Further, it is believed that the amount of unreacted materials in the specimen with higher silica content act as the defect site and has the negative effect on strength (Davidovits, 1984).

The maximum compressive strength of CFA based geopolymer was found at the mass ratio of  $Na_2SiO_3/CFA$  equal to 1.75 and thus this mass ratio of  $Na_2SiO_3/CFA$  was selected for further study.

### 4.1.2.3 Variation of curing time

After the selection of potassium hydroxide concentration (7 M) and  $Na_2SiO_3/CFA$  mass ratio (1.75), the curing time for the synthesis of geopolymer was varied from 6 to 28 days at the temperature of 40 °C. The compressive strength of geopolymeric products with the variation of curing time is shown in the following Figure 4.4:



Figure 4.4: Plot of compressive strength of CFA based geopolymeric products as a function of curing time.

The compressive strength values of 28.13, 29.81, 32.56, 34.40, 39.48 and 41.90 MPa at 6, 10, 15, 20, 25 and 28 days of curing respectively were measured of the geopolymeric products CFA. The compressive strength values increases with curing time.

Curing for longer period of time at low temperature is preferable for the synthesis of geopolymer as at low temperature condensation of geopolymer precursors and evaporation of the water molecules takes place simultaneously preventing the formation of voids and cracks inside the material thus increasing the compressive strength. It is hypothesized that hydrothermal curing is probably useful to dissolve a higher proportion of solid aluminosilicate present in the raw material that increases the extent of geopolymerisation (Kani and Allahverdi 2009 and Perera et al., 2007). The adequate curing improves mechanical and durable performances by accelerating and increasing the extent of chemical reaction (Davidovits, 1994c and 1999). This suggests that curing for longer time period at low temperature is preferable for the synthesis of geopolymer of desired higher compressive strength.

### 4.2 Demolished Cement Sand Mixture Based Geopolymer

## 4.2.1 Characterization of raw DCSM and its geopolymer products

The XRD patterns of DCSM powder of particle sizes  $\leq 53$ ,  $\leq 75$ ,  $\leq 90$  and  $\leq 120 \mu m$ , DCSM ( $\leq 53 \mu m$ ) treated with 6 M NaOH solution and Na<sub>2</sub>SiO<sub>3</sub>/DCSM mass ratio equal to 1.5 with 6 M NaOH are shown in the following Figure 4.5:



**Figure 4.5:** XRD Pattern of raw DCSM of particle size (<53 - <120 µm) and its geopolymer products.

The XRD patterns of the DCSM raw materials of various sizes in Figure 4.6 have shown the presence of mainly quartz, muscovite, rutile, calcite and silica. Though in the way of synthesis of geopolymer, use of high temperature was avoided but the raw material which were selected in the study were already treated at high temperature during their preparation. Thus muscovite and rutile may be appeared that may be due to firing of clays in order to prepare brick due to the solid state reaction at high temperature. The quartz peak ( $2\theta = 26.69^\circ$ ) was diminished with decreasing the size of particle. Several another peaks were diminished with decreasing particle size while a new peak at  $2\theta = 27.68^\circ$  was appeared which was characterized as SiO<sub>2</sub>. This was expected to be due to the conversion of quartz to silica during the process of mechanical grinding that can enhance the transformation of crystalline to amorphous phase (El-Eskandarany et al., 1997). The diminishing of several other 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 faster diffusion process (Lü and Lai, 1998). Also diminishing the XRD peaks of the raw DCSM powder treated with 6 M sodium hydroxide and Na<sub>2</sub>SiO<sub>3</sub>/DCSM = 1.5 with 6 M sodium hydroxide is due to the dissolution of alumino-silicate and the formation of geopolymeric products.

# 4.2.2 Mechanical properties of DCSM based geopolymers

## 4.2.2.1 Variation of alkali concentration

The compressive strength of DCSM based geopolymer products cured at 40 °C prepared from of particle size  $\leq$ 75 µm with the variation of alkali concentration (2 to 8 M) is shown in the following Figure 4.6:



Figure 4.6: Plot of compressive strength of DCSM based geopolymer as a function of NaOH concentration where curing time and temperature was kept constant.

The compressive strength of geopolymer products was found to be 1.03, 2.11, 2.94 and 1.95 MPa at 6 days for the sodium hydroxide concentration of 2, 4, 6 and 8 M respectively.

The plot indicates that the compressive strength initially increases upto 6 M concentration of NaOH and then decreases with further increase in the concentration of NaOH.

The reason behind the variation of compressive strength of the products is similar to those geopolymeric products obtained from coal fly ash raw material mentioned along with the references in the section 4.1.2.1 page number 52. In addition to that small size of Na<sup>+</sup> forms strong pair with small silicate oligomers and thus stabilizes the silicate monomers and dimmers, enhancing mineral dissolution of alumino-silicate promoting polymerization (Davidovits, 1988b and Yip et al., 2005).

## 4.2.2.2 Variation of particle size

The compressive strength values of geopolymer using DCSM of particle size  $\leq 53 - \leq 120$  µm treated with 6 M NaOH cured at 40 °C are shown in the following Figure 4.7:



Figure 4.7: Plot of compressive strength as a function of particle size of DCSM where alkali concentration and curing temperature was kept constant.

The compressive strength values of 3.03, 2.94, 1.18 and 0.63 MPa at 6 days of the geopolymer products DCSM were found for the particle size 53, 75, 90 and 120  $\mu$ m respectively.

The increase of compressive strength with decrease in particle size may be due to the smaller the particles size of the raw material alters the physico-chemical characteristics and thus creates surface modification which significantly increases the extent of dissolution, the reactivity and the rate of geopolymerisation (Davidovits, 1991 and Kumar et al., 2007). Furthermore, during the solidification smaller size particle formed closed packed solid.

## 4.2.2.3 Variation of Na<sub>2</sub>SiO<sub>3</sub> to DCSM mass ratio

After the selection of sodium hydroxide concentration (6 M), particle size ( $\leq$ 53 µm) of the raw material, the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/DCSM were varied between 0.5 – 2.0 and cured at 40 °C. The compressive strength values of geopolymer products with the variation of the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/DCSM is shown in the following Figure 4.8:



**Figure 4.8:** Plot of compressive strength as a function of mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/DCSM where particle size, NaOH concentration and curing temperature were kept constant.

The compressive strength values of DCSM based geopolymer products were 18.92, 27.20, 42.63, and 34.17 MPa for the mass ratio of  $Na_2SiO_3/DCSM$  equal to 0.5, 1.00, 1.50 and 2.0 respectively at 21 days.

The plot indicates that the compressive strength initially increases and then decreases with further increase in the ratio of  $Na_2SiO_3/DCSM$ . The reason behind of variation in compressive strength of the geopolymer products is similar to those geopolymeric products obtained from coal fly ash and are explained along with the references in the section 4.1.2.2 in the page number 54.

## 4.2.2.4 Variation of curing time

The concentration of sodium hydroxide of 6 M, particle size of  $\leq$ 53 µm and Na<sub>2</sub>SiO<sub>3</sub>/DCSM molar ratio of 1.5 were taken constant and the curing time were varied from 7 to 28 days at the temperature of 40 °C. The samples were removed from the oven after the required time period of curing. These samples were polished in 400 to 1500 water papers. The compressive strength values of geopolymer products are shown in the following Figure 4.9:



Figure 4.9: Plot of compressive strength of DCSM based Geopolymer as a function of curing time.

The compressive strength values of DCSM based geopolymer products were 14.00, 38.54, 42.63, and 46.95 MPa at 7, 14, 21 and 28 days respectively. The compressive strength values of the geopolymer products were found increasing with the curing time.

The plot shown in the Figure 4.9 shows the increase in compressive strength with increase in curing time. The reason behind the change in compressive strength of the products is similar to those geopolymeric products obtained from coal fly ash raw material mentioned along with references in the section 4.1.2.3 page number 55.

## 4.3 Demolished Cement Sand Concrete Mixture Based Geopolymer

### 4.3.1 Characterization of raw DCSCM and its geopolymer products

### 4.3.1.1 X-ray diffraction patterns

The raw DCSCM powder was sieved and separated into particle sizes  $\leq 53$ ,  $\leq 75$ ,  $\leq 90$  and  $\leq 120 \mu m$ . The XRD patterns of DCSCM powder of various particle sizes ( $\leq 53 - \leq 120 \mu m$ ) and its geopolymer products are shown in the following Figure 4.20:



Figure 4.10: XRD patterns of DCSCM of particle size  $\leq 53 - \leq 120 \mu m$  and its geopolymer products.

The presence of sharp peaks in the XRD patterns of the demolished cement sand concrete mixture centered at 26.6, 20.9, 51.1 and 50.1° of 2 $\theta$  angle due to the presence of quartz phase, peaks at 29.5 and 39.9 ° of 2 $\theta$  angle due to the presence of CaCO<sub>3</sub> and peak at 9.8, 27.7, 47.7 and 55.5° due to the presence of mullite, silica, anatase and rutile respectively. Though use of high temperature was avoided during the synthesis of

geopolymer but the raw material selected in the study was already treated at high temperature during their preparation. Thus mullite and rutile may be appeared due to the solid state reaction at high temperature in the manufacture of cement.

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 ( $2\theta = 26.6^{\circ}$ ) was sharpened with decreasing particle size from  $\leq 120$  to  $\leq 75 \,\mu$ m. The calcium carbonate peak ( $2\theta = 29.5^{\circ}$ ) was sharpened with decreasing particle size from  $\leq 120$  to  $\leq 90 \,\mu$ m and then diminished with further decreasing the size of particle. Several another peaks were diminished with decreasing particle size while a new peak at  $2\theta = 27.68^{\circ}$  was appeared which was characterized as SiO<sub>2</sub>. Also decrease in the several XRD peaks and increase in the amorphous nature of the sample with reducing particle size were attributed to the fact that the mechanical grinding increases the collision frequency which leads to faster diffusion process (Lü and Lai, 1998).

The diminishing XRD peaks of the raw material after treatment with NaOH and sodium silicate is due to the dissolution of alumino-silicate and the formation of geopolymer products, while some of quartz phase transform into semicrystalline phases and remained as silica after the geopolymerisation process (Lukman, 2011).

## 4.3.1.2 Chemical composition of raw DCSCM

The chemical composition of demolished cement sand concrete mixture (DCSCM) is mentioned in the following Table 4.1:

Components	Mass (%)
SiO <sub>2</sub>	58.22
$Al_2O_3$	14.28
Fe <sub>2</sub> O <sub>3</sub>	2.00
CaO	0.69
Na <sub>2</sub> O	0.21
K <sub>2</sub> O	5.11
LOI	8.76

Table 4.1: Chemical composition of demolished cement sand concrete mixture

### 4.3.1.3 SEM-EDX analysis of DCSCM based geopolymer

Microscopic imaging is one of the most important analytical techniques; scanning electron microscopy (SEM) allows visual examination on a material from millimeters to sub-micron meters which gives definitive topographical information as well as good physical and mechanical descriptions of the microstructures of crystalline as well as amorphous materials (Flewitt and Wild, 1994). The SEM images of the fractured surface of the gopolymer product DCSCM are shown in the following Figure 4.11:



Figure 4.11: SEM micrograph of DCSCM based geopolymer (a) at high magnification(b) indicating the gel formation, pores and microcracks.

From the micrographs shown above in Figure 4.11, it is observed that the geopolymer matrix comprises of compact structure, tabular gel, unreacted/partially reacted DCSCM particles along with pores and micro cracks appeared on the specimens.

SEM images observation supported by EDX analysis was used to identify the elemental composition. The average elemental analyses are presented in the Table 4.2. The EDX of the gopolymer block is shown in the following Figure 4.12: SEM micrographs observation supported by EDX analysis was used to identify the elemental composition over the seven different selected regions of the



**Figure 4.12:** The EDX analysis plot and the elemental data of EDX analysis.

geopolymer gel in the sample DCSCM. The average molar ratios by weight of seven point analysis of the geopolymer sample DCSCM were found as:  $SiO_2/Al_2O_3 = 6.85$ ,  $SiO_2/Na_2O = 1.59$ ,  $SiO_2/M_2O = 1.46$ , Si/Na = 2.00, Si/M = 1.66, Al/Na = 0.33.

EDX analysis was performed at the certain fixed point of the sample. The sample DCSCM is not a homogeneous mixture. Thus there is a difference between aggregate average and EDX analysis.

# 4.3.1.4 FTIR analysis of raw DCSCM and its geopolymer

The FTIR spectra of raw DCSCM and its geopolymer product is shown in the following Figure 4.13. The absorption band of DCSCM powder and its geopolymeric product appeared at 3420, 2360, 1630, 1430, 1020, 782, 460 and 3470, 1690, 1430, 1020, 460 cm<sup>-1</sup> respectively.



Figure 4.13: FTIR spectra of demolished cement sand concrete mixture (DCSCM) and its geopolymer product.

The bands at around 3400, 2360 and 1630 cm<sup>-1</sup> are attributed to stretching and bending vibrations of H-O-H (Zaharaki et. al., 2010 and Sadangi et al., 2013). The absorption band appeared at around 1630 cm<sup>-1</sup> shifted to 1690 cm<sup>-1</sup> were assigned to stretching (-OH) and bending (H-O-H) vibrations of bound water molecules (Bakharev, 2005 and

Fernadez and Palomo, 2005). The absorption band appeared near 1430 cm<sup>-1</sup> and was broaden in the product may be due to the stretching vibrations of the O-C-O bond indicating carbonation of the geopolymeric product (Panias et al., 2007 and Zaharaki et al., 2010). The broaden absorption band at around 1020 cm<sup>-1</sup> in the product may be due to transformation of asymmetric stretching vibrations of Si-O-Si bonds into symmetric stretching vibrations of T-O-Si (T = Si or Al) bonds and symmetric bending vibrations of Si-O-Si and O-Si-O in the geopolymer matrix (Mollah et al., 1994; Phair and Deventer, 2002 and Vempati et al., 1994). The absorption band appeared at around 782 cm<sup>-1</sup> and 461 cm<sup>-1</sup> are attributed to bending vibrations of Si-O-Si and O-Si-O bonds, implying the presence of quartz (Bakharev, 2005; Lee and Van Deventer, 2002).

The change in FTIR spectrum of raw and product were observed which are the evidence of geopolymerisation and the formation of aluminosilicate gel in geopolymeric sample.

## 4.3.2 Mechanical properties of DCSCM based geopolymer

The samples from demolished cement sand concrete mixture (DCSCM) were prepared and cured at 40 °C heating in an oven. The parameters such as alkali concentration, particle size Na<sub>2</sub>SiO<sub>3</sub>/DCSCM ratio and curing time were varied. The geopolymer obtained at 28 days of curing is shown in the following Figure 4.14:



**Figure 4.14:** Image of DCSCM based Geopolymer.

## 4.3.2.1 Variation of NaOH concentration

The geopolymer was prepared from demolished cement sand concrete mixture (DCSCM) of particle size  $\leq$ 75 µm and alkali concentrations were varied between 2 to 8 M.

The compressive strength values of geopolymer products cured at 40 °C were 1.53, 1.68, 2.21 and 1.11 MPa at 7 days for the sodium hydroxide concentration of 2, 4, 6 and 8 M respectively. This indicates that the compressive strength initially increases upto 6 M NaOH and then decreases with increasing sodium hydroxide concentration and thus 6 M NaOH were selected for further study.

The compressive strength of geopolymer products with the variation of the sodium hydroxide concentration is shown in the following Figure 4.15:



Figure 4.15: Plot of compressive strength of DCSCM based geopolymer as a function of NaOH concentration.

The variation of compressive strength of the products is due to similar reasons as that of geopolymeric products obtained from the raw materials coal fly ash and demolished cement sand mixture and are explained along with the references in the section 4.1.2.1 and 4.2.2.1 page numbers 52 and 58 respectively.

# 4.3.2.2 Variation of particle size

The particle size of the raw material was varied between  $\leq 53 - \leq 120 \mu m$ , alkali concentration of 6 M as inferred from previous work and cured at 40 °C.

The compressive strength values of geopolymer products were 3.32, 2.21, 1.45 and 1.16 MPa for the particle size  $\leq$ 53,  $\leq$ 75,  $\leq$ 90 and  $\leq$ 120 µm respectively at 40 °C for 7 days of curing.

The compressive strength values of geopolymer products with the variation of particle size are shown in the following Figure 4.16:



Figure 4.16: Plot of compressive strength of DCSCM based geopolymer as a function of particle size.

In the above plot the compressive strength increases with the decrease in particle size of the raw material. The logic behind of variation in compressive strength of the products is similar to those geopolymeric products obtained from DCSM raw materials and are elaborated along with the references under section 4.2.2.2 in the page number 59.

### 4.3.2.3 Variation of Na<sub>2</sub>SiO<sub>3</sub> to DCSCM mass ratio

After the selection of sodium hydroxide concentration (6 M) and particle size ( $\leq$ 53 µm) of the raw material, mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/DCSCM was varied.

The compressive strength values of geopolymer products were 13.80, 17.22, 45.40, 28.50, 16.00 and 18.20 MPa for the mass ratio of  $Na_2SiO_3/DCSCM$  equal to 0.5, 0.75, 1.00, 1.25, 1.50 and 2.0 respectively at 40 °C for 28 days of curing.

The compressive strength of geopolymer products with the variation of the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/DCSCM is shown in following Figure 4.17:



Figure 4.17: Plot of compressive strengths of DCSCM based geopolymer as a function of Na<sub>2</sub>SiO<sub>3</sub>/DCSCM mass ratio, at constant NaOH concentration.

The plot shown in the Figure 4.17, there is increase in compressive strength with the increase in  $Na_2SiO_3/DCSCM$  ratio, while decreases with the further increase in  $Na_2SiO_3/DCSCM$  ratio. The fact behind the change in compressive strength of the geopolymer products is similar to those of CFA and DCSM explained along with the references under the section 4.1.2.2 and 4.2.2.3 in the page numbers 54 and 60 respectively.

# 4.3.2.4 Variation of curing time

The concentration of sodium hydroxide (6 M), particle size of  $\leq 53 \mu m$ , and Na<sub>2</sub>SiO<sub>3</sub>/DCSCM = 1 were selected constant and curing time was varied between 3 - 28 days at constant temperature 40 °C. The samples were removed from the oven after the required time period. These samples were polished in 400 to 1500 water papers. The compressive strength of geopolymer products is shown in the following Figure 4.18:



Figure 4.18: Plot of compressive strength of DCSCM based geopolymer as a function of curing time.

The compressive strength values of geopolymer products were 6.25, 14.84, 25.65, 33.54 and 45.40 MPa at 3, 7, 14, 21 and 28 days of curing respectively.

The variation of compressive strength of the geopolymer products with the increase in curing time is due to the similar reasons as that of geopolymeric products obtained from the raw materials coal fly ash and demolished cement sand mixture and are elaborated along with the references along with the references in the section 4.1.2.3 and 4.2.2.4 in page numbers 55 and 61 respectively.

## 4.4 Brick Dust (K) Based Geopolymer (BD-K1)

# 4.4.1 Characterization of Brick Dust (K) and its geopolymer products

## 4.4.1.1 X-Ray diffraction patterns

The raw BD dust was sieved and separated into particle sizes  $\leq 53$ ,  $\leq 75$ ,  $\leq 90$  and  $120 \mu m$ . The XRD patterns of raw brick dust (BD-K) of various particle sizes ( $\leq 53 - \leq 120 \mu m$ ) and its geopolymer products are shown in the following Figure 4.19:



Figure 4.19: The XRD patterns of BD-K of particle size between ( $\leq$ 53 -  $\leq$ 120 µm), and its geopolymer products.

The XRD patterns of the raw brick dust have shown the presence of sharp peaks centered at 26.6 ° and 20.9 ° of 2 $\theta$  angle due to the presence of quartz phase, peak at 22.1 and 8.6 ° of 2 $\theta$  angle due to the presence of albite and muscovite phase respectively.

The peak intensity of the major peaks of quartz found to be diminished with reducing the particle size of the sample attributed to the fact that the mechanical grinding increases the collision frequency which in turn leads to faster diffusion process (Lü and Lai, 1998).

When BD was treated with NaOH and Na<sub>2</sub>SiO<sub>3</sub>-NaOH, the quartz peak was further diminished and two new peaks were appeared in case of Na<sub>2</sub>SiO<sub>3</sub>-NaOH treated BD. These two peaks were characterized as Na-muscovite  $[NaAl_2(Al,Si_3O_{10})(OH)_2]$  and Albite (NaAlSi<sub>3</sub>O<sub>8</sub>) (Gougazeh, 2013). This happens to be due to the dissolution of alumino-silicate and the formation of sodium aluminosilicate.

## 4.4.1.2 Chemical composition of raw brick powder (BD-K)

The chemical composition of brick dust (BD-K) is mentioned in the following Table 4.3:

Components	Mass (%)
SiO <sub>2</sub>	60.42
Al <sub>2</sub> O <sub>3</sub>	15.39
Fe <sub>2</sub> O <sub>3</sub>	3.21
CaO	9.14
Na <sub>2</sub> O	0.34
$K_2O$	5.37
LOI	1.10

**Table 4.3:** Chemical composition of brick powder (BD-K)

# 4.4.1.3 FTIR analysis of BD-K and its geopolymer Product

The FTIR spectra of raw brick dust and its geopolymer (BD-K2) were investigated by Fourier Transform Infrared Spectroscopy and is shown in the following Figure 4.20.



Figure 4.20: FTIR of brick dust and geopolymer product (BD-K2).

The absorption band of brick dust and its geopolymeric product (BD-K2) appeared at 3440, 1629, 1080, 782, 460 cm<sup>-1</sup> and 3460, 3137, 1641, 1460, 1400, 1065, 775, 466 cm<sup>-1</sup> respectively.

The bands at around 3400 cm<sup>-1</sup> may be due to stretching -OH (Zaharaki et. al., 2010). The band appeared at around 1629 cm<sup>-1</sup> of BD-K shifted to 1641 cm<sup>-1</sup> in the product was assigned to stretching (-OH) and bending (H-O-H) vibrations of bound water molecules. (Bakharev, 2005 and Fernadez and Palomo, 2005). The band appeared at 1425-1465 cm<sup>-1</sup> was attributed to stretching vibrations of the O-C-O bond indicating carbonation of the geopolymeric product suggesting the presence of sodium bicarbonate (Panias et al., 2007 and Zaharaki et. al., 2010). The absorption band of raw material at 1080 cm<sup>-1</sup> shifts at around 1065 cm<sup>-1</sup> was assigned to transformation of asymmetric stretching vibrations of Si-O-Si bonds into symmetric stretching vibrations of T-O-Si (T = Si or Al) bonds and symmetric bending vibrations of Si-O-Si and O-Si-O present in geopolymer matrix (Mollah et al., 1994; Phair and Deventer, 2002 and Vempati et al., 1994). The absorption band appeared at wave numbers at around 782  $\text{cm}^{-1}$  and 460  $\text{cm}^{-1}$  are ascribed to bending vibrations of Si-O-Si and O-Si-O bonds, implying the presence of quartz (Bakharev, 2005; Lee and Van Deventer, 2002). The band at 782 cm<sup>-1</sup> of the O-T-O shifted to lower wave numbers due to increased Al content in the goepolymer matrix. XRD analysis also confirmed the presence of these phases.

These observations of changes in the FTIR spectrum of the raw and the geoplymeric products indicate that the geopolymerisation reaction occurred and an aluminosilicate gel in the geopolymeric samples were observed.

## 4.4.2 Mechanical properties of (BD-K) based geopolymer (BD-K1)

### 4.4.2.1 Variation of alkali concentration

The geopolymer (BD-K1) was prepared from brick dust of particle size  $\leq$ 53 µm and alkali concentrations were varied between of 2 to 8 M. The compressive strength of geopolymer products with the variation of the sodium hydroxide concentration is shown in the following Figure 4.21:



Figure 4.21: Plot of compressive strength of brick based Geopolymer (BD-K1) and NaOH concentration.

The compressive strength values of the geopolymer products were 3.42, 3.64, 6.96 and 4.66 MPa at 7 days for the sodium hydroxide concentration of 2, 4, 6 and 8 M respectively. This indicates that the compressive strength initially increases and then decreases with increasing sodium hydroxide concentration.

The above plot in the Figure 4.21 clearly indicates increase in compressive strength with the increase in sodium hydroxide concentration upto 6 M, beyond this concentration the compressive strength decreases.

The logic behind the change is discussed along with the references in page numbers 52 and 58 under the section 4.1.2.1 and 4.2.2.1 respectively.

### 4.4.2.2 Variation of particle size

After the selection of NaOH concentration (6 M), particle sizes of the raw material (BD-K) were varied between  $\leq 53 - \leq 120 \mu m$ . The compressive strength of geopolymer products with the variation of particle size as shown in the following Figure 4.22:



**Figure 4.22:** Plot of compressive strength of brick based Geopolymer (BD-K1) as a function of particle size.

The compressive strength values of geopolymer products were 8.19, 3.86, 1.34 and 1.03 MPa at 10 days for the particle size  $\leq 53$ ,  $\leq 75$ ,  $\leq 90$  and  $\leq 120 \mu m$  respectively.

The plot shows increase in compressive strength with the decrease in particle size of the raw material. The reason behind of change in compressive strength of the products is similar to those geopolymeric products obtained from DCSM and DCSCM raw materials explained along with the references in the section 4.2.2.2 and 4.3.2.2 in the page numbers 59 and 67 respectively.

# 4.4.2.3 Variation of Na<sub>2</sub>SiO<sub>3</sub> to BD mass ratio

After the selection of sodium hydroxide concentration (6 M), particle size ( $\leq$ 53 µm) of the raw material, the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/BD-K were varied between 0.5 – 2.0.

The compressive strength of geopolymer products (BD-K1) with the variation of the mass ratio of  $Na_2SiO_3/BD$ -K is shown in the following Figure 4.23:



Figure 4.23: Plot of compressive strength of brick based Geopolymer (BD-K1) as a function of Na<sub>2</sub>SiO<sub>3</sub>/BD mass ratio.

The compressive strength values of geopolymer products was found to be 30.89, 36.67, 43.87, and 42.43 MPa at 21 days for the mass ratio of  $Na_2SiO_3/BD$ -K equal to 0.5, 1.00, 1.50 and 2.0 respectively.

In the above plot shown in Figure 4.23, the compressive strength increases with the increase in the ratio of  $Na_2SiO_3/BD$ -K, and decreases with further increase in their ratio. The logic behind the variations are similar to those of the geopolymeric products CFA, DCSM and DCSCM and are mentioned along with the references in the section 4.1.2.2, 4.2.2.3 and 4.3.2.3 in the page numbers 54, 60 and 68 respectively.

# 4.4.2.4 Variation of curing time

The concentration of NaOH (6 M), particle size of  $\leq$ 53 µm and Na<sub>2</sub>SiO<sub>3</sub>/BD-K = 1.5 was selected and curing time was varied from 7 to 28 days at temperature 40 °C. The samples were polished in 400 to 1500 water papers before the compressive strength measurement which is shown in the following Figure 4.24:



Figure 4.24: Plot of compressive strength of brick based Geopolymer (BD-K1) as a function of curing time.

The compressive strength of the geopolymer products were 12.69, 33.97, 43.87 and 60.00 MPa at 7, 14, 21 and 28 days respectively.

In the Figure 4.24, the plot clearly indicates the compressive strength increases with the increase in curing time. The logic behind such increase is similar to those geopolymer products obtained from CFA, DCSM, and DCSCM which are discussed along with the references under the section 4.1.2.3, 4.2.2.4 and 4.3.2.4 in page numbers 55, 61 and 69 respectively.

## 4.4.3 Mechanical properties of BD-K based geopolymer (BD-K2)

During the preparation of geopolymer sample (BD-K2), alkali concentration, particle size and curing temperature were varied. The geopolymer samples shown in the following Figure 4.25:



Figure 4.25: Photographs of geopolymer samples prepared from brick dust.

# 4.4.3.1 Variation of alkali concentration

The geopolymer was prepared from brick dust of particle size  $\leq 75 \mu m$  and alkali concentrations were varied between of 2 to 8 M. Then the sample was cured at 40 °C for 4 hour and then at room temperature followed by drying at 60 °C for 24 hour before compressive strength measurement and are shown in the following Figure 4.26:



Figure 4.26: Compressive strength of BD based geopolymer (BD-K2) as a function of alkali concentration.

The compressive strength of brick dust (BD) based geopolymer (BD-K2) were found to be 2.80, 3.15, 6.15 and 3.92 MPa for NaOH concentration equal to 2, 4, 6 and 8 M respectively at 7 days.

The plot clearly indicates the compressive strength increases with the increase in sodium hydroxide concentration upto 6 M beyond this concentration the compressive strength decreases. The reasons of variation are similar to other geopolymeric products CFA and DCSM and are elaborated along with the references under section 4.1.2.1 and 4.2.2.1 in page numbers 52 and 58 respectively.

## 4.4.3.2 Variation of particle size

After the selection of appropriate alkali concentration, the particle sizes of the raw materials were varied between the particle size  $\leq 75 - \leq 120 \mu m$ .

The compressive strength of brick dust (BD) based geopolymer (BD-K2) were found to be 6.15, 2.84 and 1.64 MPa at 7 days for the particle size  $\leq$ 75,  $\leq$ 90 and  $\leq$ 120 µm respectively. The compressive strength of the geopolymeric products are shown in the following Figure 4.27:



Figure 4.27: Compressive strength of brick based geopolymer (BD-K2) as a function of particle size.

In the above plot shown in Figure 4.27, the compressive strength in increase with decreasing particle size. The facts are similar to those of the geopolymeric products DCSM, DCSCM and BD-K1 and are mentioned along with the references under the section 4.2.2.2, 4.3.2.2 and 4.4.2.2 in the page numbers 59, 67 and 74 respectively.

### **4.4.3.3** Variation of curing temperature and time

The variation of compressive strength of brick dust based geopolymer sample (BD-K2) cured at 40, 50, 60 and 70 °C for 4 hour and then at room temperature for 7, 14, 21 and 28 days separately followed by drying at 60 °C for 24 hour before compressive strength measurement is shown in the Figure 4.28.

Effect of curing temperature on compressive strength curing temperature is an important factor in the setting and hardening of the geopolymer (Hardjito, 2008). 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).



Figure 4.28: Compressive strength of the geopolymer (BD-K2) as a function curing time at different temperature.

The compressive strength of brick dust (BD) based geopolymer (BD-K2) were found to be 6.15, 7.19, 11.30 and 16.70 MPa cured at 40 °C for 4 hour and then at room temperature at 7, 14, 21 and 28 days respectively, the compressive strength of brick dust (BD) based geopolymer (BD-K2) were found to be 7.44, 9.62, 15.10 and 18.60 MPa cured at 50 °C for 4 hour and then at room temperature at 7, 14, 21 and 28 days respectively, the compressive strength of brick dust (BD) based geopolymer (BD-K2) were found to be 8.71, 10.93, 18.90 and 22.70 MPa cured at 60 °C for 4 hour and then at room temperature at 7, 14, 21 and 28 days respectively and the compressive strength of brick dust (BD) based geopolymer (BD-K2) were found to be 9.40, 12.20, 19.70 and 23.47 MPa cured at 70 °C for 4 hour and then at room temperature at 7, 14, 21 and 28 days respectively. Similar results were obtained by Rovnanik, 2010; Rukzon and Chindaprasirt, 2014; Muniz-Villarreal et al., 2011; Bakharev, 2006 and Palomo et al. 1999.

From the plot it is clear that the increases in compressive strength with the increase in curing time. This variation is due to similar reasons to that of the geopolymer products obtained from CFA, DCSM, DCSCM and BD-K which are explained along with the references under the section 4.1.2.3, 4.2.2.4, 4.3.2.4 and 4.4.2.4 in page numbers 55, 61, 69 and 76 respectively.

In addition to that, the curing temperature play significant role in the synthesis of geopolymers, it not only acts as accelerators of chemical reaction, but also determines the extent of the reaction (Davidovits, 1999 and Hardjito et al., 2008).

# 4.5 Brick Dust and Sand Cement Waste Based Geopolymers

## 4.5.1 Characterization of BD-K, SCW and its geopolymer products

### 4.5.1.1 X-ray diffraction patterns

The XRD patterns of brick dust, dolomite and its geopolymer product (BD-K3, SCM and BDSCM) are shown in the following Figure 4.29:



Figure 4.29: XRD patterns of geopolymer samples obtained from various starting materials.

Major peaks of the brick dust at  $2\theta = 21.36$ , 27.18, 50.70, 60.50 and 68.75° were that of quartz silica and the major peak of dolomite at  $2\theta = 30.07$ , 36.63, 40.05, 43.81, 48.21 and 49.17° were mostly the peaks of CaCO<sub>3</sub> and MgCO<sub>3</sub>.

These peaks were also found diminished on treating with the alkaline activator solution. This is due to the dissolution of silica in the presence of alkaline activator also addition of a little CaO significantly improved the formation of geopolymer network by their complete incorporation of the Na and Ca atoms into geopolymer structure (Temuujin et al., 2009b).

## 4.5.2 Mechanical properties of geopolymers (BD-K3, SCM and BDSCM)

### 4.5.2.1 Variation of alkali concentration

The geopolymer was prepared from the waste brick dust (BD) and sand cement mixture (SCM) of particle size  $\leq$ 75 µm and alkali concentrations were varied between of 2 to 8 M. The compressive strength of geopolymer products with the variation of the sodium hydroxide concentration is shown in the following Figure 4.30:



**Figure 4.30:** Plot of compressive strength of the geopolymeric products (SCM and BD-K3) with a variation of alkali concentration.

The compressive strength of geopolymeric products (SCM) were found to be 1.2, 2.1, 2.5, 2.9, 1.9 and 1.5 MPa for the sodium hydroxide concentration of 2, 4, 5, 6, 7 and 8 M respectively at 7 days of curing at 40 °C, and the compressive strength of geopolymeric products (BD-K3) were found to be 3.1, 3.7, 4.6, 6.7, 4.5 and 4.3 MPa for the sodium hydroxide concentration of 2, 4, 5, 6, 7 and 8 M respectively at 7 days of curing at 40 °C.

In the above plot, the compressive strength increases upto 6 M NaOH then decreases with the further increase in concentration of NaOH. These variations of compressive strength of the products are similar to other geopolymeric products which are explained along with the references under the section 4.1.2.1 and 4.2.2.1 in the page numbers 52 and 58 respectively.

## 4.5.2.2 Variation of particle size

After the selection of sodium hydroxide concentration (6 M), particle sizes of the raw material were varied between  $\leq 75 - \leq 120 \mu m$ . The compressive strength of geopolymeric products with the variation of particle size are shown in the following Figure 4.31:



**Figure 4.31:** Compressive strength of the geopolymeric products (SCM and BD-K3) with a variation of particle size.

The compressive strength of geopolymeric products SCM and BD-K3 were found to be 2.9, 2.3, 1.2 and 6.7, 4.5, 2.1 MPa at 7 days of curing at 40 °C for the particle size  $\leq$ 75,  $\leq$ 90 and  $\leq$ 120 µm respectively.

The plot shown in Figure 4.31, with the decrease in particle size the compressive strength increases. The reason behind such increase in compressive strengths are similar to those of the geopolymeric products DCSM, DCSCM and BD-K1 which are elaborated along with the references in the section 4.2.2.2, 4.3.2.2 and 4.4.2.2 in the page numbers 59, 67 and 74 respectively.

## 4.5.2.3 Variation of dolomite percentage

After the selection of sodium hydroxide concentration (6 M), particle size of the raw material ( $\leq$ 75 µm), variation of dolomite percentage between 10 – 50% were carried out. The compressive strength of geopolymeric products SCM and BD-K3 with the variation of dolomite percentage are shown in the following Figure 4.32:


**Figure 4.32:** Compressive strength of the geopolymeric products (SCM and BD-K3) with a variation of dolomite composition.

The compressive strength of geopolymer products (SCM) were found to be 3.3, 5.2, 9.7, 5.0 and 2.9 MPa for the dolomite percentages of 10, 20, 30, 40 and 50 respectively, and the compressive strength of geopolymer products (BD-K3) were found to be 5.7, 9.2, 11.9, 7.5 and 5.3 MPa for the dolomite percentages of 10, 20, 30, 40 and 50 respectively.

The increase in compressive strength may be due to decrease in porosity as well as accumulation of calcium compounds CaO and Ca(OH)<sub>2</sub> which improves the mechanical properties. In fly ash-based geopolymer cured at ambient temperature lime stone dust have been utilized as an additive, had showed an improvement in the mechanical properties (Temuujin et al., 2009b; Dutta and Ghosh, 2012).

The plot indicates that the compressive strength increases upto 30 percentage dolomite addition and then decreases. Therefore 30 percent of dolomite was selected.

#### 4.5.2.4 Variation of curing time

The alkali concentration of 6 M, particle size of  $\leq$ 75 µm, dolomite addition of 30 percentage and mixture of BD and SCM in the ratio of 60:40 was taken to be constant and curing time was varied. The curing time of geopolymer products (SCM, BD-K3 and BDSCM) were varied from 7 to 28 days at the temperature of 40 °C.

The compressive strength of the geopolymeric products SCM and BD-K3 were found to be 9.7, 23.0, 29.8, 36.3 and 11.9, 26.5, 36.3, 45.1 MPa at 7, 14, 21 and 28 days respectively. And the compressive strength of the geopolymeric products (BDSCM) obtained from mixture of brick dust and sand cement waste were found to be 10.3, 24.1, 33.7, and 43.2 MPa at 7, 14, 21 and 28 days respectively. The compressive strength of geopolymer products is shown in the following Figure 4.33:



**Figure 4.33:** Compressive strength of the geopolymeric products (SCM, BD-K3 and BDSCM) prepared from BD and mixing of BD and SCM with a variation of curing time.

The above plot indicates that the compressive strength values increases with curing time. This variation is due to similar reasons of the geopolymer products obtained from CFA, DCSM, DCSCM and BD-K which are elaborated along with the references in the section 4.1.2.3, 4.2.2.4, 4.3.2.4 and 4.4.2.4 in page number 55, 61, 69 and 76 respectively.

#### 4.6 Brick Dust (J) Based Geopolymer Products

# 4.6.1 Characterization of raw BD-J and its geopolymer products

# 4.6.1.1 X-ray diffraction patterns

The XRD patterns of powder BD-J, geopolymer product BDAM, BDMK and BDL are shown in the following Figure 4.34:



Figure 4.34: XRD patterns of brick powder (BD-J), geopolymer products BDAM, BDMK and BDL.

Major peaks of the brick dust at  $2\theta = 20.82$ , 26.62, 36.51, 39.43, 42.44 and 50.12 ° were that of quartz silica.

In case of geopolymer product BDL, the presence of lime along with alkaline activator solution significantly improved the physical as well as the mechanical properties. This may be due to the incorporation of the Na and Ca atoms into geopolymer structure (Temuujin et al., 2009b). The SEM micrographs of the geopolymer BDMK (Figure 4.42) clearly showed that the microstructures were very different and have impact on the physical and mechanical properties. The XRD pattern from the geopolymer BDMK was found to have some aluminosilicate hydrate gel formation (Temuujin et al., 2009c).

## 4.6.1.2 Particle size distribution of ball-milled brick (BD-J)

The characteristics particle size distribution of BD-J milled for half an hour, one hour, one and half hour and two hour respectively are shown in the following Figure 4.35:



**Figure 4.35:** Plot of cumulative particle size distribution of ball-milled (for 30 – 120 minute) BD-J powder.

The characteristics particle diameters, specific area density and as a function of milling time are mentioned in the following Table 4.4:

**Table 4.4:** Characteristics particle diameter and specific surface area of brick powder milled for different time.

Milling time (min)	d <sub>10</sub> (μm)	d <sub>50</sub> (μm)	d <sub>90</sub> (μm)	Specific surface area (m <sup>2</sup> /g)	Specific gravity (g/cm <sup>3</sup> )
30	1.82	24.06	82.65	0.9162	2.7028
60	0.94	13.96	53.55	1.3804	2.6852
90	0.68	10.60	44.71	1.6442	2.6765
120	0.53	8.32	40.86	1.9148	2.5279

The particle size gradually decreased and the specific surface area of the sample BD-J increases with milling time. Particle size reduction alters the physico-chemical characteristics and thus creates surface modification which can significantly alter the reactivity of solids (Kumar et al., 2007). The smaller the particle size of the starting material the higher the reactivity and the geopolymerisation rate (Davidovits, 1991).

## 4.6.1.3 Chemical composition of raw brick dust (BD-J)

The chemical compositions of raw materials are mentioned in the following Table 4.5:

Radicals (%)	$SiO_2$	$Al_2O_3$	$Fe_2O_3$	CaO	Na <sub>2</sub> O	$K_2O$	LOI <sup>*</sup>
BD-J	65.1	13.41	8.591	3.33	3.25	4.06	1.96
Metakaolin	56.26	36.74	0.38	0.13	0.16	0.082	3.02
lime	1.52	-	-	72.09	-	-	22.3

**Table 4.5:** Chemical composition of the raw material BD-J, Metakaolin and lime.

\*Loss on ignition

# 4.6.1.4 Isothermal conduction calorimetric (ICC) analysis

ICC plots of brick (BD-J) treated with 6 M NaOH were carried out using additives such as metakaolin and lime are shown in the following Figure 4.36:



Figure 4.36: Cumulative plot of heat of reaction of different composition of BD-J powder with 6M NaOH.

Isothermal conduction calorimetric plots of brick (BD-J) treated with 1:1 solution of 6 M NaOH and sodium silicate solution were carried using additives such as metakaolin and lime are shown in the following Figure 4.37:



**Figure 4.37:** Cumulative plot of heat of reaction of different composition of BD-J with (1:1) solution of 6M NaOH and sodium silicate.

Isothermal calorimetric analysis shown that the raw material was not much reactive, addition of hydrated lime and Metakaolin was selected to improve the mechanical and microstructural properties of the geopolymer. Addition of 4 percent industrial grade lime and 10 percent metakaolin separately by weight was selected. In the previous work, additions of calcium hydroxide and metkaolin have shown to decrease in the setting time as well as accelerate the early stage reaction that results in the improvement of geopolymerisation (Khater. 2012 and Bentz et al., 2012). Since the raw material was fine having particle size ( $d_{50}$ ) of was 24.06, 13.96, 10.60 and 8.32 µm of brick powder ballmilled for 30, 60, 90 and 120 minute respectively. From the Figure 4.36 and 4.37, it in inferred that the activation in 1:1 solution of 6M NaOH and sodium silicate is more reactive than in presence of only 6M NaOH. The orders of reactivity of different composition of brick powder are found as: BDAM < BDL < BDMK.

The heat of hydration is the filling of porosity with hydration products that is chiefly responsible for strength development in cement-based materials. Each unit of heat release corresponds to a specific volume of hydration products that fills in the initially available pore space and should therefore contribute to strength development (Bentz et al., 2012).

#### 4.6.1.5 Physical properties of the geopolymer products

Water absorption is an important property that influences the durability of the building unit i.e., block. The lower value of water absorption indicates higher resistance to water infiltration and to environmental damage. Water absorption, apparent porosity and bulk density were Test carried at 28 days as per ASTM C373 standards and are mentioned in Table 4.6. From the results, the water absorption values are less than (17 %), a limit of ASTM C90 standard specification for load bearing masonry units.

Sample	Apparent Porosity (%)	Water Absorption (%)	Bulk Density
BDL-A	28.24	15.88	1.77
BDL-B	26.56	14.97	1.80
BDL-C	25.18	13.55	1.86
BDL-D	23.48	12.56	1.88
BDMK-A	21.89	12.26	1.67
BDMK-B	21.32	11.9	1.72
BDMK-C	21.30	11.5	1.74
BDMK-D	19.8	11.07	1.75

 Table 4.6:
 Characteristics Water absorption, Apparent porosity and Bulk density of geoplolymer at 28 days of curing.

The samples of A-2, B-2 and BDAM were not stable when boiled, there is loss in mass and these test could not performed successfully.

### 4.6.1.6 SEM-EDX analysis of BD-J based Geopolymers

The formation of aluminosilicate phase in the geopolymeric products was also confirmed from the SEM micrograph of the of the geopolymeric products B-2, BDAM, BDL and BDMK.

#### **Geopolymer Sample B-2**

The scanning electron micrographs (SEM) of the geopolymer products B-2 are shown in the following Figure 4.38:



**Figure 4.38:** (a) SEM micrograph of geopolymer product B-2 at high magnification (b) SEM micrograph of B-2 indicating the gel formation and pores

From the micrographs shown above in the Figure 4.38, it is observed that the morphology of geopolymer product B-2 obtained have tabular as well as fibrous type gel along with some pores and partially reacted brick dust particles. This fibrous type of morphology is expected to be due to the formation and nucleation of quartz phase.

SEM micrographs observation supported by EDX analysis was used to identify the elemental composition is shown in the following Figure 4.39 and the average elemental analysis of the geopolymer sample B-2 is shown in the following Table 4.7: The elemental analysis over the seven different selected regions of the geopolymer gel in the geopolymer sample B-2 was identified by SEM-EDX analysis. The average ratios of seven point analysis

	Element	Wz %	At %
3 -	0	19.79	31.46
	Na	04.26	04.72
0 -	Al	07.24	06.82
Cot Si	Si	55.18	49.97
	к	03.07	02.00
6 -	Ca	01.48	00.94
	Fe	08.99	04.09
3 - 1 A			
Ha Ca	Fe		

**Figure 4.39:** The EDX analysis plot of geopolymer product B-2 and the elemental data of EDX analysis.

were found as:  $SiO_2/Al_2O_3 = 8.4$ ,  $SiO_2/Na_2O = 18.59$ ,  $SiO_2/M_2O = 11.60$ , Si/Al = 7.32, Si/Na = 10.5, Si/M = 6.79, Al/Na = 1.68, Al/M = 0.93.

## **Geopolymer Sample BDAM**

The scanning electron micrographs (SEM) of the geopolymer product BDAM are shown in the following Figure 4.40:



**Figure 4.40:** (a) SEM micrograph of geopolymer BDAM at high magnification (b) SEM micrograph of BDAM representing the gel formation, pores and partially/unreacted.

From the micrographs shown in the Figure 4.40, it shows that the geopolymer matrix

comprises of tabular gel particularly aluminosilicate hydrate (ASH) and calcium silicate hydrate (CSH) also supported by FTIR data, partially reacted brick dust particles along with large volume of pores appeared on the specimen.

The average elemental analysis of the geopolymer product BDAM shown in the Table 4.8 which was identified by SEM-EDX micrographs observation shown in the



EDX micrographs observation shown in theFigure 4.41: EDX analysis plot of geopolymerfollowing Figure 4.41: To identify the elementalBDAM and the elemental data of EDX analysis.

composition over different selected region. The average molar ratios were determined over seven different point analysis of gel formed in the geopolymer sample BDAM were found as:  $SiO_2/Al_2O_3 = 10.23$ ,  $SiO_2/Na_2O = 7.98$ ,  $SiO_2/M_2O = 6.88$ , Si/Al = 5.12, Si/Na = 3.92, Si/M = 3.37, Al/Na = 0.77, Al/M = 0.67.

## **Geopolymer Sample BDMK:**

Figure 4.42 shows the morphology of brick (BD-J) based geopolymer products BDMK.



**Figure 4.42:** (a) SEM micrograph of geopolymer BDMK at high magnification (b) SEM micrograph of BDMK representing the gel formation, pores and partially/unreacted particles.

The micrographs shown above in the Figure 4.42, it clearly shows that the geopolymer matrix consists of tabular gel particularly aluminosilicate hydrate (ASH) and calcium

silicate hydrate (CSH) also indicated by FTIR data, The micrograph indicates unreacted or partially reacted brick particles along with some pores are appeared at the fractured surface of the specimen.

SEM images observation supported by EDX analysis shown in the Figure 4.42: was used to identify the elemental composition of the geopolymer product



**Figure 4.43:** The EDX analysis plot of geopolymer BDMK and the elemental data of EDX analysis.

BDMK and are shown in the following Table 4.9: The elemental composition over seven different selected regions of the geopolymer gel in the sample BDMK was identified by SEM micrographs observation supported by EDX analysis. The average molar ratio of seven point analysis of gel in the geopolymer product BDMK were:  $SiO_2/Al_2O_3 = 6.65$ ,  $SiO_2/Na_2O = 8.17$ ,  $SiO_2/M_2O = 7.39$ , Si/Al = 3.33, Si/Na = 3.98, Si/M = 3.62, Al/Na = 1.19, Al/M = 1.09.

# **Geopolymer Sample BDL:**

The scanning electron micrographs (SEM) of the geopolymer product BDL are shown in the following Figure 4.44:



**Figure 4.44:** (a) SEM micrograph of geopolymer BDL at high magnification (b) SEM micrograph of BDL representing the compact structure, gel formation, pores and microcracks.

The micrographs shown in the Figure 4.44 shows the morphology of the geopolymer matrix comprises of compact structure, tabular gel particularly aluminosilicate hydrate (ASH) and calcium silicate hydrate (CSH) also supported by FTIR data, unreacted/partially reacted brick dust particles along with some pores and also micro cracks are appeared on the specimen.

The average elemental composition of the geopolymer product BDL is shown in the Table 4.10 that was identified by SEM-EDX analysis shown in the following Figure 4.45:

SEM-EDX analysis was used to identify 3.1 the elemental composition over the seven 2.5 regions different selected of the geopolymer gel in the sample BDL. The 1.9 KCnt average molar ratios of seven point 1.2 analysis of geopolymer gel in the sample BDL were:  $SiO_2/Al_2O_3$ = 12.18, 0.6  $SiO_2/Na_2O = 14.18$ ,  $SiO_2/M_2O = 10.61$ , 0.0 Si/Al = 9.93, Si/Na = 7.26, Si/M = 5.45, Al/Na = 1.21, Al/M = 0.91.



**Figure 4.45:** EDX analysis plot of geopolymer BDL and the elemental data of EDX analysis.

# 4.6.1.7 FTIR analysis of raw brick dust (BD-J) and its geopolymers

The FTIR spectra of brick dust (BD-J) and the geopolymer products B-2, BDAM, BDMK and BDL are shown in the following Figure 4.46:



Figure 4.46: FTIR spectra of brick dust (BD-J), geopolymer sample BDAM, BDMK and BDL.

The FTIR absorption band of brick dust (BD-J) appeared at 3428, 2358, 1890, 1627, 1084, 784, 690, 460 cm<sup>-1</sup>. The absorption band of the geopolymeric products appeared at 3428, 2360, 1648, 1463, 1084, 784, 460 cm<sup>-1</sup>.

Absorption band at around 3400 and 2360 cm<sup>-1</sup> is attributed to the stretching vibrations of -OH and at around 1630 cm<sup>-1</sup> is bending vibrations of H-O-H (Zaharaki et al., 2010). In the raw material the band at around 1627 cm<sup>-1</sup> shifted to 1648 cm<sup>-1</sup> may be due to the stretching (-OH) and bending (H-O-H) vibrations of bound water molecules. (Bakharev, 2005; Fernadez and Palomo, 2005), this indicates the existence of intense -OH and H<sub>2</sub>O peaks and are attributed to the water released during condensation step of geopolymerization.

The absorption band appeared at around 1425-1465 cm<sup>-1</sup> may be due to the stretching vibrations of the O-C-O bond indicating carbonation of the geopolymeric product which indicates the presence of sodium bicarbonate (Panias et al., 2007 and Zaharaki et al., 2010). In the raw material the absorption band at around 1080 cm<sup>-1</sup> became wider and shifted towards lower wave number region in the geopolymeric products BDAM, BDMK and BDL was assigned to the transformation of asymmetric stretching vibrations of Si-O-Si bonds into symmetric stretching vibrations of T-O-Si (T = Si or Al) bonds and symmetric bending vibrations of Si-O-Si and O-Si-O present in geopolymer matrix indicating the formation of new Al-Si phases due to structural reorganization in the geopolymeric matrix (Kumar et al., 2007). These differences of wave numbers appeared are related to the fingerprint of the geopolymerisation (Phair and van Deventer, 2002), as they confirm the dissolution of the raw solid materials during geopolymeric products (Fernadez and Palomo, 2005; Lee and van Deventer, 2002 and Maragkos et al., 2008).

The band appeared at around 775-800 cm<sup>-1</sup> and 460 cm<sup>-1</sup> are ascribed to bending vibrations of Si–O–Si and Si–O/Al-O bonds respectively also may be due to the presence of quartz (Bakharev, 2005; Lee and van Deventer, 2002; Phair and van Deventer, 2002). XRD analysis also confirmed the presence of these phases. From these observations, the changes in the FTIR spectrum of raw and geopolymeric products indicates the occurrence of geopolymerisation reaction and thus the formation of aluminosilicate gel in these geopolymeric samples.

## 4.6.2 Mechanical properties of BD-J based geopolymer

The samples BDAM, BDMK and BDL prepared and cured at  $32\pm3$  °C and kept for four hour followed by heating in oven at 60 °C for next 24 hour for 3-28 days. The geopolymer samples were subjected for drying treatment at 60 °C for 24 h before the measurement of compressive strength so as to improve the mechanical properties. Geopolymer samples BDAM, BDMK and BDL are shown in the following Figure 4.47:



Figure 4.47: Brick (BD-J) based geopolymer products (a) BDAM (b) BDMK and (c) BDL for compressive strength measurement.

#### 4.6.2.1 Compressive strength of the geopolymer sample A-2 and B-2

The geopolymer was prepared from brick dust (BD-J) of different milling time (30 - 60 minute) and 1:2 solution of 6 M NaOH and liquid sodium silicate to synthesized the geopolymer products A-2 and B-2 curing for 7 - 28 days. The compressive strength of these samples is shown in the Figure 4.48.

The compressive strength of the geopolymer products (A-2 and B-2) were found to be 6.75, 8.44, 9.40, 10.59 MPa and 9.70, 9.89, 10.55, 11.43 cured at 60 °C for 24 hrs followed by curing at room temperature ( $32\pm3$  °C) for 7, 14, 21 and 28 days respectively.



Figure 4.48: Compressive strength of brick (BD-J) based geopolymer products A-2, B-2 with variation of milling time.

The compressive strength of the geopolymers obtained from the brick dust of Jamshedpur was found lower than that of brick dust of Kathmandu. This is expected due to the different nature of clays used and curing temperature. Furthermore, the salt contents within the clay and soil samples in moving from north to south in our region increases due to the variation of altitude and distance from sea level. Also some supporting evidences can be seen from the chemical analysis data of both types of brick dusts shown in the table 4.3 and 4.5 in pages 72 and 89 respectively.

With the increase of the curing time the compressive strength of all samples was found increasing. The compressive strength values of B-2 type geopolymer product obtained from higher milling time were found higher than those obtained from lower milling time A-2. Such trends in the compressive strengths variation of the samples give the indication that the improvement in strength and is related with the variation of milling time and the amount of sodium silicate (Kumar and Kumar, 2011; Lloyd and Rangan, 2010).

#### 4.6.2.2 Compressive strength of the geopolymer sample BDAM

The geopolymer was prepared from brick dust BD-J (A, B, C and D) of different milling time (30 - 120 minute) and 1:1 solution of 6 M NaOH and liquid sodium silicate to synthesized the geopolymer products BDAM-A, BDAM-B, BDAM-C and BDAM-D curing for 3 - 28 days. The compressive strength of these samples is shown in the following Figure 4.49:



Figure 4.49: Plot of compressive strength of geopolymer BDAM with variation of milling time.

The compressive strength of geopolymer product BDAM-A prepared from brick dust (BD-J) milled for 30 minute were found to be 3.80, 4.22, 5.70.5.77 and 5.80 MPa at 3, 7, 14, 21 and 28 days respectively. The compressive strength of geopolymer product BDAM-B prepared from brick dust (BD-J) milled for 60 minute were found to be 3.97, 5.72, 6.10, 6.20 and 6.45 MPa at 3, 7, 14, 21 and 28 days respectively. The compressive strength of geopolymer product BDAM-C prepared from brick dust (BD-J) milled for 90 minute were found to be 4.11, 5.78, 6.80, 6.98 and 7.18 MPa at 3, 7, 14, 21 and 28 days respectively. And he compressive strength of geopolymer product BDAM-D prepared from brick dust (BD-J) milled for 120 minute were found to be 5.20, 6.80, 7.92, 8.31 and 8.35 MPa at 3, 7, 14, 21 and 28 days respectively.

In each case the compressive strength increases with the reduction of particle size which is attributed due to higher rate of dissolution (Kumar and Kumar, 2011 and Temuujin, 2009). Also the result shows in agreement with the work conducted by Kumar et al., 2012 i.e., reduction in particle size showed slightly higher strength. However vibratory milling results an improvement of compressive strength of upto 50 percent (Provis, 2010).

## 4.6.2.3 Compressive strength of the geopolymer sample BDMK

The geopolymer was prepared from brick dust BD-J (A, B, C and D) of different milling time (30 - 120 minute). In order to improve the strength of the product 10 percent of metakaolin was added to prepare the geopolymer products BDMK-A, BDMK-B, BDMK-C and BDMK-D and curing time was varied for 7 - 28 days. The compressive strength of these samples is shown in the Figure 4.50:

The compressive strength of geopolymer product BDMK-A prepared from brick dust (BD-J) milled for 30 minute were found to be 12.04, 12.49, 13.60 and 14.48 MPa at 7, 14, 21 and 28 days respectively. The compressive strength of geopolymer product BDMK-B prepared from brick dust (BD-J) milled for 60 minute were found to be 16.20, 16.29, 16.45 and 17.80 MPa at 7, 14, 21 and 28 days respectively. The compressive strength of geopolymer product BDMK-C prepared from brick dust (BD-J) milled for 90 minute were found to be 17.91, 18.16, 18.40 and 19.60 MPa at 7, 14, 21 and 28 days respectively. And he compressive strength of geopolymer product BDMK-D prepared

from brick dust (BD-J) milled for 120 minute were found to be 18.88, 19.91, 20.02 and 21.30 MPa at 7, 14, 21 and 28 days respectively.



Figure 4.50: Plot of compressive strength geopolymer products BDMK with variation of milling time.

The reason behind this increase of compressive strength values of the geopolymeric products is similar to those of geopolymer product BDAM. Also the addition of metakaolin increases the compressive strength value of the geopolymer products BDMK. The change in geopolymerisation reactions may be due to combined effect of increase in surface area and change in reactivity due to the addition of metakaolin. This is due the acceleration of the condensation reaction by releasing aluminium ions from metakaolin and its incorporation into calcium silicate hydrate (Wassing, 2008 and Buchwald, 2009).

# 4.6.2.4 Compressive strength of the geopolymer sample BDL

The geopolymer prepared from BD-J (A, B, C and D) of different milling time (30 - 120 minute). The compressive strength of which are shown in the following Figure 4.51: The compressive strength of geopolymer product BDL-A prepared from brick dust (BD-J) milled for 30 minute were found to be 8.14, 9.90, 11.20, 14.05 and 14.56 MPa at 3, 7, 14, 21 and 28 days respectively.



Figure 4.51: Plot of compressive strength of geopolymer products BDL with variation of milling time.

The compressive strength of geopolymer product BDL-B prepared from brick dust (BD-J) milled for 60 minute were found to be 8.53, 10.90, 11.57, 14.80 and 16.87 MPa at 3, 7, 14, 21 and 28 days respectively. The compressive strength of geopolymer product BDL-C prepared from brick dust (BD-J) milled for 90 minute were found to be 10.25, 12.90, 15.84, 18.90 and 21.32 MPa at 3, 7, 14, 21 and 28 days respectively. And he compressive strength of geopolymer product BDL-D prepared from brick dust (BD-J) milled for 120 minute were found to be 13.36, 18.30, 19.70, 22.05 and 25.00 MPa at 3, 7, 14, 21 and 28 days respectively.

The logic behind this increase of compressive strength values of the geopolymeric products is similar to those of geopolymer product BDAM and BDMK. The variation in geopolymerisation reactions was due to combined effect of decrease in particle size of the raw material, change in reactivity due to the addition of lime that results the formation of compact structure. The result shows in agreement with the work conducted by the addition of CaO have positive effects on the compressive strength of geopolymer (Xu and Deventer, 2000). It has been reported that the accumulation of calcium compounds CaO and Ca(OH)<sub>2</sub> improves mechanical properties (Temuujin et al., 2009b). In fact the high

CaCO<sub>3</sub> content effects in quicker geopolymerisation and the development of semicrystalline Ca-Al-Si gel. Thus incorporation of Ca ion in the geopolymer skeleton plays significant role (Yip and van Deventer, 2001).

## 4.6.3 Flexural strength of the geopolymer sample BDAM, BDMK and BDL

Flexural strength is a measure of tensile strength of concrete. It is used to examine the ability to bend the material without obtaining any major deformities. The flexural strength is expressed as psi or MPa. Generally flexural strength is about 10 to 20 percent of the compressive strength depending upon the type, size and volume of the coarse aggregate used in the sample. A schematic diagram of measuring the flexural strength of the geopolymer sample is shown in the following Figure 4.52:



Figure 4.52: Schematic diagram of flexural strength measurement

A standard experiment as per ASTM C 293, three-point test was used to calculate flexural strength of the material by using the formula:  $Flexural strength = \frac{3LW}{2BD^2}$ 

The brick based geopolymer samples (length: breadth: height =  $160 \text{ mm} \times 40 \text{ mm} \times 40$  mm) BDAM, BDMK and BDL were prepared for flexural strength testing is shown below in the following Figure 4.53:



Figure 4.53: Brick (BD-J) based geopolymer products (a) BDAM (b) BDMK and (c) BDL for flexural strength measurement.

The flexural strength of the geoolymer sample BDAM, BDL and BDMK at 28 days cured at 60 °C for 24 hour followed by  $32\pm3$  °C by is shown in the following Figure 4.54:



**Figure 4.54:** Plot of flexural strength of the geopolymer samples (BDAM, BDMK and BDL) with variation of milling time.

The flexural strength of geopolymer sample BDAM prepared from BD-J (A, B, C and D) was found to be 1.92, 2.18, 2.21 and 2.31 MPa respectively at 28 days of curing. For the geopolymer sample BDL prepared from BD-J (A, B, C and D) were found to be 2.78, 3.06, 3.26 and 3.32 MPa respectively at 28 days. For the geopolymer sample BDMK prepared from BD-J (A, B, C and D) were found to be 2.34, 2.50, 2.64 and 2.75 MPa respectively at 28 days. Flexural strength found to be increases with the increase in milling time of brick dust due to mechanical activation (Kumar et al., 2008).

#### 4.7 Secondary Data Analysis

#### 4.7.1 Variation of compressive strength with Si/Al atomic ratio

The compressive strength values of the geopolymer products with the variation of Si/Al ratio is indicated in the following Figure 4.55:



Figure 4.55: Plot of compressive strength with respect to Si/Al ratio.

The compressive strength values of the geopolymer products decreases with increasing Si/Al ratio, at low Si/Al ratio the system referred to as poly(sialate) geopolymers. For Si/Al  $\geq$  3.16 the compressive strength values found decreasing. Similar results were obtained in previous work (Zheng et al., 2010). This may due to the fact that at low Si/Al ratio, increase in tetrahedral Al incorporation into the silicate backbone. Further increase of silica, decreases the rate of geopolymerisation reaction and the solidification of the paste takes place prior to geopolymerisation (Provis and van Deventer, 2007).

#### 4.7.2 Variation of compressive strength with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mass ratio

The compressive strength values of the geopolymer products with the variation of  $SiO_2/Al_2O_3$  ratio is indicated in the following Figure 4.56, the compressive strength values of the geopolymer products increased with the decrease in  $SiO_2/Al_2O_3$  ratio.



Figure 4.56: Plot of compressive strength with respect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio.

The increase in compressive strength values may be due to higher dissolution of SiO<sub>2</sub> to facilitate the geopolymerisation process. Similar trend in case of metakaolin based geopolymer is reported. An optimum SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 5.01 was favorable for the production of high strength geopolymer, beyond to a certain limit (De Silva et al., 2007). However this ratio is not very critical particularly when dealing with waste materials. This is due to the fact that the compositional ratio is based on chemical analysis although it is highly unlikely that all of the silica or alumina actually takes part in the reaction (van Jaarsveld, 1996). The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio also found to be responsible for high-strength gains at later stage upto a certain limit, however below it i.e., for very low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, led to products of low strength (De Silva et al., 2007).

### 4.7.3 Variation of compressive strength with Na<sub>2</sub>O/SiO<sub>2</sub> mass ratio

The compressive strength of the geopolymer products with the variation of  $Na_2O/SiO_2$  ratio is indicated in the following Figure 4.57:



Figure 4.57: Plot of compressive strength with respect to Na<sub>2</sub>O/SiO<sub>2</sub> ratio.

With the increasing in the ratio of  $Na_2O/SiO_2$  activator up to 0.58, the compressive strength of the geopolymer products increases and reaches to 45.4 MPa after 28 days of curing at 40 °C. This may be due to the dissolution of raw material particles and gelation of AlO<sub>4</sub> and SiO<sub>4</sub> species to reach the complete formation of gel structure, similar results also have been reported (Soleimani et al., 2012).

A study on the  $Na_2O/SiO_2$  ratio and water sorptivity had showed at lower alkali content. i.e., at high  $Na_2O/SiO_2$  ratio sorptivity decreases that enhances the mechanical properties (Ghosh and Ghosh, 2012).

#### 4.7.4 Variation of compressive strength with Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio

The compressive strength of the geopolymer products with the variation of  $Na_2O/Al_2O_3$  ratio is indicated in the following Figure 4.58:



Figure 4.58: Plot of compressive strength with respect to Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio.

With the increase in the ratio of  $Na_2O/Al_2O_3$  from 0.23 to 0.66, the compressive strength values of the geopolymer products decreases sharply. While further increase of  $Na_2O/Al_2O_3$  ratio equal to 3.2, the compressive strength values decreases marginally.

The higher values of compressive strength at low  $Na_2O/Al_2O_3$  ratio may be due to the incorporation of higher positive charge on Al in the form of aluminate exists as  $[Al(OH)_4]^-$  with tetrahedral structure which is more likely to attract the negatively charged OH<sup>-</sup> from alkali, it has four hydroxyl groups (Weng, 2005).

The decrease in compressive strength values with increasing ratio of  $Na_2O/Al_2O_3$  may be due the incorporation of alkali molecule between two geopolymer precursors which break the silicon anion connectivity thus preventing polymerization (Singh et al., 2005).

#### 4.7.5 Variation of compressive strength with Na<sub>2</sub>O/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) mass ratio

The compressive strength of the geopolymer products with the variation of  $Na_2O/(SiO_2+Al_2O_3)$  ratio is indicated in the following Figure 4.59:



Figure 4.59: Plot of compressive strength with respect to  $Na_2O/(Al_2O_3+SiO_2)$  ratio.

The Figure 4.53 shows that compressive strength values of geopolymer products increase with increasing  $Na_2O/(SiO_2+Al_2O_3)$  ratio, i.e., it shows the dependence of NaOH concentration, the increase in compressive strength may be due to higher dissolution of aluminosilicate to facilitate the geopolymerisation. Similar result has been reported in previous work conducted on fly ash based geopolymer (Muduli et al., 2013).

In the case with the decrease in  $Na_2O/(SiO_2+Al_2O_3)$  ratio, the compressive strength increases. In facts this ratio is not very critical particularly when dealing with waste materials. This is due to the fact that the compositional ratio is based on chemical analysis although it is highly unlikely that all of the silica or alumina actually takes part in the reaction (van Jaarsveld, 1996).

CHAPTER 5 CONCLUSIONS

## **5.1 Conclusions**

The geopolymerisation behaviour of construction and demolition wastes such as coal fly ash (CFA), demolished sand cement mixture (DCSM), demolished cement sand concrete mixture (DCSCM) and brick dust (BD) were studied. These wastes contain aluminosilicate in significant amount. It was found that use of 6 M NaOH is suitable for geopolymerisation, decrease in particle size, increase in temperature and curing time increases the mechanical strength of the geopolymer products.

A compressive strength values of 6.62, 28.07 and 41.90 MPa were obtained with CFA treated with 7 M KOH solution, mass ratio of  $Na_2SiO_3$  to CFA equal to 1.75 at 4, 4 and 28 days respectively of curing.

A compressive strength values of 3.03, 42.63, and 46.95 MPa were obtained with DCSM treated with 6 M NaOH solution, mass ratio of Na<sub>2</sub>SiO<sub>3</sub> to DCSM equal to 1.5 for the particle size of DCSM  $\leq$ 53 µm at 6, 21 and 28 days respectively of curing and that of DCSCM ( $\leq$ 53 µm particle size) based geopolymer treated with 6 M NaOH solution, mass ratio of Na<sub>2</sub>SiO<sub>3</sub> to DCSCM equal to 1.0 were 3.32 and 45.40 MPa at 7 and 28 days respectively of curing.

The compressive strength values of brick dust (BD-K,  $\leq$ 53 µm particle size) based geopolymer product (BD-K1) treated with 6 M NaOH, mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/BD-K equal to 1.5 were 8.19 and 60.00 MPa at 40 °C for 10 and 28 days respectively of curing.

The compressive strength values of brick dust (BD-K,  $\leq$ 75 µm particle size) based geopolymer (BD-K2) with 1:1 solution 6 M NaOH and liquid sodium silicate was found to be 9.40, 12.20, 19.70 and 23.47 MPa at 28 days of curing at 40, 50, 60 and 70 °C respectively.

A compressive strength values of the geopolymer products BD-K3, SCM and BDSCM obtained from brick dust and sand cement dust ( $\leq$ 75 µm particle size) and their mixture in the ratio of 60:40 along with 30% of dolomite treating with Na<sub>2</sub>SiO<sub>3</sub>.5H<sub>2</sub>O was dissolved

in 6 M NaOH was found to be 36.30, 45.10 and 43.20 MPa at 28 days respectively of curing at 40  $^{\circ}$ C.

The maximum compressive strength of brick dust (BD-J) based geopolymer products A-2 and B-2 treated with 1:2 solution 6 M NaOH and liquid sodium silicate was found to be 10.59 and 11.43 MPa cured at 60 °C for 24 hrs followed by curing at room temperature  $(32\pm3 \text{ °C})$  for 28 days respectively.

The maximum compressive strength of brick dust (BD-J) based geopolymer products BDAM, BDMK and BDL treated with 1:1 solution 6 M NaOH and liquid sodium silicate was found to be 8.35, 21.30 and 25.00 MPa cured at 60 °C for 24 hrs followed by curing at room temperature ( $32\pm3$  °C) for 28 days respectively.

From the secondary data analysis, the compressive strength values were found to be maximum at Si/Al ratio equal to 3.16, with the further increase in the ratio, the compressive strength values were found to be decreasing. A similar trend of result was found from the plot of compressive strength against SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mass ratio. A maximum compressive strength was found at Na<sub>2</sub>O/SiO<sub>2</sub> mass ratio equal to 0.58, below this ratio the compressive strength found to decrease. A lower Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio was found favorable, a maximum compressive strength was found at Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 0.23.

Addition of metakaolin has increased the reactivity and a compressive strength of to 21.30 MPa was achieved at 28 days of curing. Further addition of lime improved the geopolymerisation reaction and the compactness of the geopolymer product and a compressive strength of 25 MPa were achieved at 28 days. The strength development is related to formation of two types of gel phases: one is ASH and second is CSH. This is related to dense gel formation corresponding to ASH gel. Thus formed amorphous Al-Si phase was revealed according to XRD and FTIR analysis and detected through SEM analysis of the obtained materials.

The excellent physical and mechanical properties of the produced inorganic polymeric materials were attributed to the formation of an amorphous aluminosilicate gel phase, in

which the non-dissolved particles of the raw solid materials were well bonded. Thus construction and demolition waste materials coal fly ash, demolished cement sand mixture, demolished cement sand concrete mixture and brick dust (CFA, DCSM, DCSCM, BD) can be used for the synthesis of geopolymer and are suitable for building application that may be synthesized with addition of suitable admixtures such as CaO or metakaolin etc.

The study may significantly contribute the substantial reduction in environmental disruption by reducing the consumption of cement thus reducing  $CO_2$  emission, reducing precious land, and the use of natural resources.

The products manufactured from these wastes comprises materials in form of brick, block, tiles, plate, concrete etc, which possess sufficient mechanical strength, low porosity and water absorption, heat and acid resistance properties. These products are suitable for use in road building and other constructional activities including construction of heat and acid resistance structures. The materials made up by chemical activation of fly ash along with other additives are also useable for encapsulation and fixation of various toxic constituents of polluting solid wastes in making rock forming bodies for safe disposal.

Establishment of geopolymerisation as a feasible technology for the management of construction and demolition waste will contribute to considerable saving in disposal costs, recycling of wastes, substantially reduces the greenhouse gas emissions and hence socially accepted. It will be an important step towards sustainable development of the nation.

## **5.2 Limitations**

There is a safety risk associated with the high alkalinity of the activating solution. The high alkalinity requires more processing, resulting in increased energy consumption and greenhouse gas generation.

The polymerisation reaction is sensitive to temperature and the geopolymer concrete requires to be cured at slightly elevated temperature under a strictly controlled temperature. The extreme alkalinity of inorganic polymers, which may be a drawback in some applications, can be offset by heating to about 600 °C, thereby fixing the alkali within the structure (MacKenzie et al., 2010).

X-ray fluorescence spectroscopy was not available and therefore chemical analyses of the materials in bulk phase were not performed in the earlier stage of the study. Also FTIR spectra and, SEM-EDX of the samples CFA, BD-K1, BD-K3, SCM and BDSCM were not obtained due to the unavailability of instrumental facilities at Central Department of Chemistry, Tribhuvan University.

While measurement of compressive strength of the prepared geopolymer sample, availability of sample was restricted to minimum sample size of 5 cm  $\times$  5 cm  $\times$  5 cm cube at Nepal Standards and Metrology, Government of Nepal which was difficult to carry out in this study, because it requires large amount and much more time to prepare the sample as it was prepared manually.

CHAPTER 6

# SUMMARY AND RECOMMENDATION FOR FURTHER WORK

## 6.1 Summary

Construction and demolition waste (CDW) is priority waste in European Union countries. It is emerging as one of the major waste worldwide that requires sustainable solution. Utilization of CDW is getting increased attention as it is mainly waste of urban area where no land is available for disposal. There is a significant potential for recycling and utilizing construction and demolition waste for the use in value added applications and provides an alternative construction materials to maximize economic and environmental benefits.

In the present study four types of construction and demolition wastes were selected which were coal fly ash (CFA), demolished cement sand mixture (DCSM), demolished cement sand concrete mixture (DCSCM), bricks from Kathmandu (BD-K) and Jamshedpur (BD-J).

The compressive strength values of the geopolymer products were ranges from 8.35 to 60.00 MPa (NaOH, 6M; particle size,  $\leq$ 53 µm and Na<sub>2</sub>SiO<sub>3</sub>/BD-K = 1.5) at 28 days of curing at ambient temperature (40 °C).

In case of temperature variation, the compressive strength values of the geopolymer products (BD-K2) found increasing from 9.40 to 23.47 MPa at 28 days of curing for 40 and 70 °C respectively for four hour followed by curing at room temperature ( $12\pm3$  °C).

Use of additives such as metakaolin and lime enhanced the compressive strength of brick based geopolymer products from 8.35 to 21.30 and 25.00 MPa respectively at 28 days of curing for the samples BDAM, BDMK and BDL.

The compressive strength values were found to be maximum at Si/Al ratio equal to 3.16, with the further increase in the ratio, the compressive strength values were found to be decreasing. A similar trend of result was found from the plot of compressive strength against  $SiO_2/Al_2O_3$  mass ratio. A maximum compressive strength was found at  $Na_2O/SiO_2$  mass ratio equal to 0.58, below this ratio the compressive strength found to

decrease. A lower Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio was found favorable, a maximum compressive strength was found at Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 0.23.

Characterization of geopolymer was carried out through XRD, SEM-EDX and FTIR strength based analysis. The higher strength development of the sample BDL is related to formation of two types of gel phases, one is aluminosilcate hydrate and the other is calciumsilicate hydrate. The increase in strength of the sample BDMK is related to the formation of aluminosilicate hydrate gel.

For the applications of high strength based products, the geopolymer products are seemed to have less strength than conventional cement based products but the strength and durability of the geopolymer products can be enhanced in further studies. For relatively lower or medium strength based applications of cement materials, geopolymer material can give best alternate. Furthermore geopolymers are eco-friendly and environmentally friendly alternate for conventional cement products.

The aim of present study was based on complete utilization of CDW through scientific understanding on the geopolymerisation behavior of CDW. The geopolymerisation behavior of CDW activated by alkali and alkali silicate solution and the change in chemical reactivity at ambient temperature was studied using isothermal conduction calorimeter. From the above study geopolymer material suitable for building application may be synthesized from brick dust with addition of suitable admixtures such as CaO or metakaolin.

# 6.2 Safety and Precautions

- 1. During dust handling, preparation of activator solution, use of spectacle, mask, gloves and apron should not be avoided.
- 2. After casting the sample, the presence of air bubbles should be removed by tapping.
- 3. During the preparation of alkali solution and activator, use of glassware should be avoided.

## **6.3 Recommendations**

Attempt has been made to correlate the structure with properties in this study during synthesizing geopolymer from construction and demolition waste, alkali and sodium silicate, while much information regarding the characters and the properties of these materials has been elucidated. Future work should be undertaken to gain a better understanding about the physical and mechanical properties together with several applications of the geopolymers. The following recommendations are made for the future work:

- The inclusion of calcium from calcium disilicates Ca(H<sub>2</sub>SiO<sub>4</sub>) or some other sources into geopolymer precursors which is expected to create calciumaluminsilicate in the geopolymer matrix.
- Geopolymer concretes with similar size to those in OPC and PPC concretes need to be considered, to get a direct comparison of the physical, mechanical, thermal, durability, environmental resistivity as well as economical standpoint.
- 3. A detail study of the new applications of geopolymer products such as electronic properties, catalytic activities, photoactive applications, biological functionalities etc. will facilitate the geopolymer chemistry in future course of time.
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SCIENTIFIC PUBLICATIONS

## **Appendix A: Scientific Publications**

- Arvind Pathak, Sanjay Kumar and Vinay Kumar Jha, (2014), Development of Building Material from Geopolymerization of Construction and Demolition Waste (CDW), *Transactions of the Indian Ceramic Society*, 73(2), 133-137.
- Arvind Pathak, Nirmal Pokharel and Vinay K. Jha, (2014), A Green Building Material from Demolition Waste, Proceedings of International Conference on Technology and Innovation Management, 127-130.
- Arvind Pathak and Vinay K. Jha, (2013), Comparative study of the Geopolymers Synthesized from Various Types of Construction Wastes, *Nepal Journal of Science* and Technology, 14(1), 81-86.
- Arvind Pathak, Ambar B. Rangumagar, Dipak Paudel, Rishi B. Bhandari and Vinay K. Jha, (2012), Synthesis and Characterization of Geopolymer from Various Types of Construction Wastes, *proceedings of International Conference on Technology and Innovation Management*, 93-101.
- Ambar B. Rangumagar, Arvind Pathak and Vinay K. Jha, (2012), A Laboratory Scale Synthesis of Geopolymer from Brick-Dust Waste, *The Journal of University Grants Commission, Nepal,* 1(1), 58-67.
- Dipak Paudel, Arvind Pathak and Vinay K. Jha, (2012), A Laboratory Scale Synthesis of Geopolymer from Demolished-Cement-Sand-Mixture, *Journal of Nepal Geological Society*, 44, 83-88.
- Arvind Pathak and Vinay K. Jha, (2012), Synthesis of Geopolymer from Inorganic Construction Waste, *Journal of Nepal Chemical Society*, 30, 45-51
- Rishi B. Bhandari, Arvind Pathak and Vinay K. Jha, (2012), A Laboratory Scale Synthesis of Geopolymer from Locally Available Coal Fly Ash from Brick Industry, *Journal of Nepal Chemical Society*, 29, 18-23.

## **Appendix B: Conference/Seminar/Workshop Attended**

- Development of Building Material Through Geopolymerization of Construction and Demolition Wastes (CDW) (Oral presentation), 16<sup>th</sup> International Symposium on Eco-materials Processing and Design (ISEPD-2015), (Organized by Nepal– Materials and Environmental Studies and Research Consultancy (MESRC) and Prism Consults International Lab (PCIL)), held in Kathmandu, Nepal on January 12-15, 2015.
- Scientific writing and publishing workshop (Participated), organized by Progressive Sustainable Developers Nepal (PSD-Nepal) in collaboration with National Institute of Environmental Health Sciences (NIEHS), NC, USA held in Kathmandu, Nepal on November 3-4, 2014.
- A Green Building Material from Demolition Waste (Oral presentation), Technology Innovation Management, International Conference-2014" (Organized by CARD, Dept. of Mechanical Engineering IOE, NTNU and FNCCI) held in Kathmandu, Nepal on October 10-12, 2014.
- Green Building Material From Geopolymerisation Of Construction And Demolition Waste (CDW) (Poster presentation), National Science Day at B. P. Koirala Planetorium (Organized by Ministry of Science and Technology) held in Kathmandu, Nepal on September 17-18, 2014.
- 5. Geopolymer (a building material) Synthesis from Alkaline Activation of Construction and Demolition Wastes (CDW) (Oral presentation), Kathmandu Symposia on Advanced Materials (KαSAM)-2014 Organized by Nepal Polymer Institute in co-operation with Tribhuvan University, Kathmandu University, University of Rouen, France held in Kathmandu, Nepal on September 7-10, 2014.
- Development of Building Material from Geopolymerization of Construction and Demolition Wastes (Oral presentation), International Conference on Ceramic Science (Organized by Indian Ceramic Society) held in Jamshedpur, India on December 19-20, 2013.

- Synthesis and Characterization of Geopolymer from Various Types of Construction Wastes (Oral presentation), Technology Innovation Management, International Conference-2012 (Organized by CARD, Dept. of Mechanical Engineering IOE, NTNU and FNCCI) held in Kathmandu, Nepal on October 10-12, 2012.
- Laboratory Scale Synthesis of Geopolymer from Various Construction Wastes (Oral presentation), Sixth National Conference on Science and Technology (Organized by Nepal Academy of Science and Technology) held in Kathmandu, Nepal on September 25-27, 2012.
- Exploring the possibility of Geopolymer synthesis from various types of construction wastes (Oral presentation), Chemical Constellation Cheminar-2012 (Organized by Dr. B R Ambedkar National Institute of Technology) held in Jalandhar, India on September 10-12, 2012.
- Laboratory Scale Synthesis of Geopolymer from Various Construction Wastes (Oral presentation) in Kathmandu Symposia on Advanced Materials (KαSAM)-2012 Organized by Nepal Polymer Institute in co-operation with Tribhuvan University, Kathmandu University, University of Rouen, France sponsored by International Union of Pure and Applied Chemistry (IUPAC) held in Kathmandu, Nepal on May 9 -12, 2012.
- Kathmandu 2012 Workshop on Theoretical Chemistry (Participated) organized under Honorary Patron Hon'ble Prof. Vishwanath P. Agrawal held in Kathmandu, Nepal on 30 April – 4 May, 2012 Kathmandu, Nepal.
- 12. Synthesis of Geopolymer from Inorganic Construction Waste (Oral presentation) in International Conference on Advanced Materials and Nanotechnology for Sustainable Development (Organized by Nepal Chemical Society in Co-operation with Central Department of Chemistry, Tribhuvan University) held in Kathmandu, Nepal on October 21-23, 2011.



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## Development of Building Material from Geopolymerization of Construction and Demolition Waste (CDW)

Arvind Pathak,<sup>1</sup> Sanjay Kumar<sup>2</sup> and Vinay Kumar Jha\*

Central Department of Chemistry Kirtipur, Kathmandu, Nepal

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Construction and demolition waste (CDW) which is produced during new construction, renovation and demolition of buildings and other construction structures is considered priority waste and is generated several million tons globally. India generates 15-23 million tons per year. The recycling and utilization of CDW would be a significant contribution to the environment and sustainable development towards the adoption of "zero waste" principle. One of the promising technologies to convert industrial waste into value added product is geopolymerization and it involves a chemical reaction between solid alumino-silicate oxides and alkaline activator solution at ambient or slightly elevated temperatures. The product thus obtained has high mechanical strength. Two types of CDW, i.e. concrete powder and brick powder, were considered in the present study. Calorimetric analysis showed that brick dust is more reactive than concrete waste. The maximum compressive strength of geopolymer product from brick dust was found 11.43 MPa. It was found that the physico-mechanical properties of geopolymers obtained from CDW were comparable with the properties of equivalent building materials. The structural changes in resulting geopolymer were studied using XRD, FTIR and SEM-EDX.

[Keywords: Construction and demolition waste, Geopolymerization, Alkaline activator]

#### Introduction

Construction and demolition waste (CDW) is priority waste in European Union countries. It is emerging as one of the major wastes worldwide. Reuse of CDW is getting increased attention as it is mainly waste of urban area where no land is available for disposal. Two major fractions of CDW which comprise about 70% of total CDW are: (a) ceramic waste (includes bricks, tiles, plaster, etc) and (b) concrete waste (includes hydrated cement, sand, aggregate, etc). The first category has the potential for developing new building materials whereas the second has the potential for recycling.

Population growth, increasing urbanization, uplifting of life-style due to technological innovations have contributed to an increase in the quantity of construction and demolition wastes. It is generated whenever any construction/ demolition activity takes place, such as, building roads, bridges, fly-over, subway, remodeling, etc. The CDW has become a global concern that requires sustainable solution. There is significant potential for recycling and utilizing construction and demolition waste for use in value added applications and provides an alternative construction material to maximize economic and environmental benefits. This would also contribute to control and reduce the release of undesirable gases and pollutants to the environment. Recycling potential of solid waste, such as construction

<sup>1</sup>Additional affiliation: <sup>1</sup>Department of Chemistry, Tri-Chandra Multiple Campus, Ghantaghar, Kathmandu, Nepal debris, marble processing into building material (waste and their recycling potentials) has been studied and reported.<sup>1</sup> However, some quantity of such waste is being recycled and utilized in building materials; dust is usually dumped on the riverbeds and this possesses a major environmental concern.<sup>2</sup> In dry season, the marble powder/dust dangles in the air, flies and deposits on vegetation and crop. All these significantly affect the environment and local ecosystems. Fine particles result in poor fertility of the soil due to increase of its alkalinity.<sup>1</sup>

The effect of clay-brick-powder (CBP) on concrete mechanical properties was studied and the compressive and flexural strengths more than 50 and 10 MPa respectively for 28 days of curing were reported.<sup>3</sup> The potential of geopolymer technology towards green buildings and future sustainable cities by utilizing several wastes or by-products, such as coal combustion ashes, metallurgical slags, construction and demolition wastes for the production of geopolymer concrete and construction component have been studied.<sup>4</sup>

A key strategy of construction waste management is recycling, which could offer the following benefits: (i) reducing demand for new resources, (ii) cutting down transport and production energy cost, (iii) utilizing waste which would otherwise be lost to landfill sites, (iv) preserving areas of land for future urban development and (v) improving the general state of environment.<sup>5, 6</sup>

Geopolymerization is emerging as an energy efficient and ecofriendly process to develop building materials from varieties of waste. Ceramic waste, which is alumino-silicate in composition, can be used as potential feedstock for

<sup>\*</sup>Corresponding author; e-mail: vinayj2@yahoo.com

<sup>&</sup>lt;sup>2</sup>CSIR-National Metallurgical Laboratory, Jamshedpur, India

geopolymer synthesis. The alkaline activation of construction and demolition waste is a chemical process that allows transforming glassy structures (partially or totally amorphous) into well compact cemented composites. It is a relatively new technology that transforms alumino-silicate materials into geopolymer, which involves a chemical reaction between solid alumino-silicate and an alkaline activation solution at ambient or slightly elevated temperatures, yielding an amorphous to semi-crystalline polymeric structure with Si-O-AI and Si-O-Si bonds.<sup>7-15</sup>

Geopolymerization can be approximately partitioned into two periods: (I) dissolution-hydrolysis, (II) hydrolysispolycondensation. These two steps occur simultaneously once the solid material is mixed with liquid activator. The exact separation of these two steps is possible from the point of view of thermodynamics.<sup>16</sup> Glukhovisky<sup>17</sup> proposed a general mechanism for alkali activation of material primarily comprising silica and reactive alumina. The process involves three steps: (a) destruction-coagulation, (b) coagulation-condensation, (c) condensation-crystallization. The other proposed mechanism of geopolymerization in alkali-metakaolin system is: (1) deconstruction (dissolution of metakaolin in alkaline solution), (2) polymerization (of alumina/silica-hydroxyl species and oligomers), and (3) stabilization (small gels formed are transformed into large networks through reorganization).<sup>18</sup>

The construction and demolition waste and brick powder are the rich source of alumino-silicate while these materials create problem due to their unplanned deposits. The main objective of the present study is to utilize these waste materials for the synthesis of geopolymer and to characterize the obtained materials through various instrumental techniques.

### Experimental

The raw material used in the present study was construction and demolition waste, particularly brick, which was obtained from the demolished garbage site of the residence of National Metallurgical Laboratory (NML), Agrico, Jamshedpur. It was divided into small pieces, pulverized and then ball-milled for half an hour (sample A), and one hour (sample B). The particle size analysis of brick dust milled for different time was carried out by laser particle size analyzer (MASTERSIZER S. Malvern, UK). The rate of heat evolution during the reaction (dg/dt) at 27°C was measured using an eight channel isothermal conduction calorimeter (TA AIR, Thermometric AB, Sweden). 7 g sample was taken in ampoule and 4 mL 1:1 solution of 6M NaOH-sodium silicate was used separately; the mixture was then mixed and loaded in the channel of calorimeter. X-ray diffractometer (Bruker, Germany) using CuKa radiation was used for phase analysis of the samples. A scanning speed of 1.5°.min<sup>-1</sup> was used and the samples were scanned from 10°-80° (20). Morphological characterization of the fractured samples was done 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. FTIR samples were obtained by mixing with KBr.

For the synthesis of geopolymer from brick powder, 100 g of each type of brick powder ( $^{1}/_{2}$  h and 1 h ballmilled) was taken separately and varying amounts of NaOH, water glass and water were mixed in it. The mixing ratio of brick dust, NaOH, water glass and water is shown in Table I. The mixtures were separately kept in mould (5 × 5 × 5 cm<sup>3</sup>) and cured at 60°C for 24 h. The samples were then removed from the moulds and kept for different time durations at 32°±3°C (room temperature at the time of present work was in the range 30°-35°C). Finally, the compressive strength of thus obtained geopolymer products was measured on an Automatic Compression Testing machine (AIMIL COMPTEST 2000, India).

Table I : Amounts (g) of brick dust, NaOH, water glass and water used for the preparation of geopolymer

Sample	Brick dust	NaOH	Water glass	Water
A-1	100	3.56	20.16	20.95
B-1	100	3.56	20.16	20.95
A-2	100	2.37	26.87	20.42
B-2	100	2.37	26.87	20.42

## Results and Discussion Characterization of Raw Brick Dust

There was slight difference in colour of the two samples of brick powder ball-milled for  $^{1}\!/_{2}$  h and 1 h separately. Sample B was less brownish which may be due to the difference in particle size. The specific gravities of sample A and sample B were 2.53 and 2.68, respectively. The chemical composition of the milled brick powder is given in Table II. Figure 1 shows typical particle size distributions of sample A and sample B. The specific surface areas of sample A and sample B were 0.92 and 1.38 m<sup>2</sup>.g<sup>-1</sup> respectively. Based on median particle size D<sub>50</sub>, the particle diameters of sample A and sample B were 24.06 and 13.96  $\mu$ m respectively.

Table II:	Chemical	composition	(mass%)	of	milled	brick	powder
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SiO <sub>2</sub>	65.30		
Al <sub>2</sub> O <sub>3</sub>	13.45		
$Fe_2O_3$	8.62		
CaO	3.34		
Na <sub>2</sub> O	3.26		
K <sub>2</sub> O	4.07		
LOI*	1.97		
*Loss on ignition			



Fig. 1 – Typical particle size distributions of the brick powders, ball-milled for different time durations

#### Compressive Strength Development of Geopolymer

The plot of the compressive strength of all the four types of samples against varied curing times is shown in Fig. 2. The compressive strength of the geopolymer products from brick dust was found to vary between 4.22 and 11.43 MPa. With the increase of the curing time the compressive strength of all the samples was found to increase. The strengths of A-1 and A-2 type samples were found lower than those of B-1 and B-2 types respectively. Furthermore, the strengths of A-2 and B-2 type samples were higher than those of A-1 and B-1 samples respectively.

Such trend in compressive strength variation of the samples give the indication that the improvement in strength is related to the milling time as well as to the amount of sodium silicate.<sup>19, 20</sup>



Fig. 2 – Variation of compressive strength of geopolymers synthesized from brick dust with activator

#### XRD Analysis of Geopolymer Sample

XRD patterns of brick dust and its geopolymer products with 1:1 and 1:2 6M NaOH and sodium silicate solutions are shown in Fig. 3. Major peaks of the brick dust at  $2\theta = 20.8$ , 26.7, 50.1, 59.9 and 68.1 were that of quartz silica (JCPDS card no. 46-1045), which were



Fig. 3 – XRD patterns of (a) brick dust, (b) geopolymer prepared from brick dust and 1:1 6M NaOH and sodium silicate solution, (c) geopolymer prepared from brick dust and 1:2 6M NaOH and sodium silicate solution

found to be little diminished after treating with NaOH and sodium silicate. This is due to the dissolution of silica in presence of alkali solution in it. The additional XRD peaks of brick dust after treating with NaOH and sodium silicate at  $2\theta = 27.4$ , 36.6, 39.5 and 45.8 were that of sodium aluminium silicate hydroxide hydrate (JCPDS card no. 46-1457). These peaks were also found to get diminished on treating with NaOH and excess sodium silicate. This is due to the dissolution of silica in the presence of alkali solution in it and formation of more geopolymer network.

#### Isothermal Conduction Calorimetric Analysis

Isothermal calorimetric plots of concrete, brick sample A and brick sample B treated with 1:1 solutions of 6M NaOH and sodium silicate are shown in Fig. 4. The heat of hydration is the filling of porosity with hydration products that is chiefly responsible for strength development in cement-based materials. Each unit of heat release corresponds to a specific new volume of hydration products that fills in the initially available pore space and should therefore contribute to strength development.<sup>21</sup>



Fig. 4 – Cumulative heat of hydration of brick sample A-1, B-1 and concrete sample C-1 (for comparative study) with 1:1 solutions of 6M NaOH and sodium silicate

The greater heat of hydration indicates greater dissolution of alumino-silicate species and larger polymeric network formation. The greater cumulative heat of hydration of brick samples B-1 and A-1 than concrete sample C-1 indicates their reactivity of the following trend:

Concrete powder < Brick sample-A < Brick sample-B.

### FTIR Analysis

The FTIR spectra of brick dust, geopolymer samples B-1 and B-2 are shown in Fig. 5. The bands at 455-460 cm<sup>-1</sup> was related to Al–O/Si–O in plane and bending modes, 775 and 798 cm<sup>-1</sup> may be due to octahedral and tetrahedral Al-O stretching modes.<sup>19</sup> The absorption bands at 1081.8, 1081.9 and 1085.7 cm<sup>-1</sup> may be due to asymmetric stretching of Al-O and Si-O bonds present in geopolymer matrix. The broad shoulder centered at 1081.9-1085.7 cm<sup>-1</sup> is assigned to longitudinal optical mode (Si-O-Si). The absorption band at around 1465 cm<sup>-1</sup> is either due to carbonation or presence of Na<sub>2</sub>CO<sub>3</sub> in the geopolymer sample. The slight shifting and change in intensity of the peaks may be due to the structural reorganization in geopolymer matrix.<sup>22</sup>

The broadening and reducing the intensities of the peaks appearing at 1081.9-1085.7, 455-460, 775 and 798 cm<sup>-1</sup> were expected to be due to the dissolution of alumino-silicates and the formation of geopolymer network.



Fig. 5 – FTIR spectra of brick dust, geopolymer samples B-1 and B-2  $\,$ 

### SEM-EDX Analysis

Scanning electron micrographs (SEM) of brick dust milled for 1 h and treated with 1:1 and 1:2 solutions of 6M NaOH and sodium silicate (B-1 and B-2, respectively) together with their corresponding geopolymer products are shown in Fig. 6.

SEM-EDX analysis showed that the morphology of the obtained geopolymer product having slightly lower Si/AI ratio (2.60 in case of B-1 geopolymer and 1.84 in case of B-2 geopolymer) was of tabular gel type, shown as G, while that with higher Si/AI ratio (2.99 in case of B-2 geopolymer)



Fig. 6 – SEM images of brick dust milled for 1 h and treated with 1:1 and 1:2 solutions of 6M NaOH and sodium silicate (B-1 and B-2 respectively) together with their corresponding geopolymer products

was of fibrous type, shown as F. This fibrous type of morphology is probably due to the formation and nucleation of quartz phase. There is much more unreacted portion (indicated by A) in sample B-1 than in B-2; the higher reactivity of sample B-2 than B-1 is indicated by the fibrous type gel formation.

### Conclusions

Brick powder has shown the reactivity with alkali activator; the maximum compressive strengths developed after 28 days are 5.80, 6.45, 10.45 and 11.43 MPa, which is related to loose packed gel formation corresponding to alumino-silicate hydrate gel. Geopolymer material suitable for building applications may be synthesized from brick dust.

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

## Arvind Pathak and Vinay Kumar Jha

Central Department of Chemistry, Tribhuvan University, Kathmandu e-mail: vinayj2@yahoo.com

## 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 CO<sub>2</sub>, about 3 kg of Nitrogen Oxide (NO<sub>x</sub>), an air contaminant that contributes to ground level smog and 0.4 kg of PM10 (particulate matter of size 10  $\mu$ m), an air borne particulate matter that is harmful to the respiratory tract when inhaled. The global release of CO<sub>2</sub> from all sources is estimated at 23 billion tons a year and the Portland cement production accounts for about 7% of total CO<sub>2</sub> emissions. The cement industry has been making significant progress in reducing CO<sub>2</sub> emissions through improvements in process technology and enhancements in process efficiency, but further improvements are limited because CO<sub>2</sub> 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 aluminsilicate 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 beings 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 alumino-silicate 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, Panias 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 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  $CO_2$ 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 μm to d"120 μm 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<sub>2</sub>SiO<sub>3</sub> 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  $^{\circ}\mathrm{C}.$ 

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<sub>2</sub>), 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  $2\dot{e} = 26.6^{\circ}$  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) sandcement-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) sandcement-mixture (SCM) and (c) concrete-mixture CM construction wastes treated with 6 M NaOH solution.

# Variation of Na<sub>2</sub>SiO<sub>3</sub> to construction waste mass ratio

The compressive strength of geopolymer products with the variation of the mass ratio of  $Na_2SiO_3$ : 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  $Na_2SiO_3$ : 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  $Na_2SiO_3$ : BD and SCM.



**Fig. 4.** Variation of the mass ratio of Na<sub>2</sub>SiO<sub>3</sub>/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 alumino-silicate 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 geoplymer 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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