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EFFECT OF ALKALI CONCENTRATION ON THE PREPARATION OF VOLCANIC MUD AND QUARRY DUST BASED GEOPOLYMER

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Abstract

The volcanic mud sample was collected from Yauk Chaung Village, Kyaukphyu Township, Rakhine State and quarry dust from Loikaw Township, Kayah State. The physical properties (moisture content, loss - on -ignition, specific gravity ,fineness, pH and pozzolanic reactivity) of volcanic mud and quarry dust samples were determined and characterized by conventional and modern spectroscopic methods (EDXRF, XRD and SEM).From the EDXRF and XRD analysis, it was observed that the major oxide compositions were present as SiO_2, CaO, Fe_2O_3 and Al_2O_3 in both samples. It was found that the samples were silica-alumina rich compound. From the SEM micrographs, the microstructure of quarry dust appeared to be glassy, hollow and porous structure . In the microstructure of volcanic mud sample, the micrograph indicates crystalline nature. It can be considered that the pores are micro-porosity sized particles. The optimum conditions of sodium hydroxide concentration and the ratio of sodium hydroxide and sodium silicate which are used in the preparation of geopolymer have been determined. The physical properties (apparent porosity, water absorption, apparent density) and the mechanical properties (compressive strength) of prepared volcanicmud based geopolymer were also determined. Compressive strength of geopolymer ranged from 6.70 to 21.41N/mm^2.The mechanical properties compressive strength of prepared volcanic mud-quarry dust based geopolymer (GP) and blended cement (GP: Cement) (1:1, 1:2, 2:1) at different time intervals (7, 14 and 28 days) have been determined.

Keywords: Geopolymer, compressive strength, blended cement, pozzolanic reactivity

Introduction

The global warming problem caused by CO_2 became one of the serious international environmental issues to be solved. In particular, the CO_2 produced in the manufacturing process of Portland cement used in most building and civil constructions are increasing every year. 0.4 ~ 1.0 tons of CO_2 were produced to make 1 ton of cement and it is as much serious as 7% of total CO_2 amount of global production were used for making cement.

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Therefore, many researchers have focused on reducing CO_2 production and substitute materials for cement with the consideration of ecological industry in the future. The prospecting materials for non-sintering inorganic binders are fly ash, slag and brick powder from the industrial wastes as well as natural raw materials such as clay and incinerated kaolin (Mc Lellan *et al*., 2011).

The development of geopolymer concrete is an important step towards the production of environmentally friendly concrete. The name geopolymer was formed by a French Professor Davidovits in 1978 to represent a broad range of materials characterized by networks of inorganic molecules. The fundamental chemical and structural characteristics of geopolymer derived from metakaoline, fly ash and slag are explored in terms of the effects of raw material selection on the properties of geopolymer composite (Mc Lellan et al., 2011).

Geopolymers are novel class of materials that are formed by the polymerization of silicon, oxygen and aluminium species to form an amorphous three-dimensional framework structure (Kyi Kyi San,2013). Geopolymerization can transform a wide of waste alumino-silicate materials into building and mining materials with excellent chemical and physical properties, such as fire and acid resistance (Palomo *et al*,1999).

Reuse of various industrial by-products such as flyash, silicafume, rice husk ash foundry waste, quarrydust, et cetera as substitutes to the conventional construction materials in construction has been atgued to be a possible way forward towards achieving an environmentally friendly construction (Neville,2002; Gambhir,1995). Most common alkali activator used in geopolymerization is a combination of NaOH or KOH and Na_2SiO_3 .(Khin Moe Aye,2013).

Geopolymer can be synthesized by the condensation of Si^{4+} and Al^{3+} ions came from the industrial wastes or natural ores by alkaline activators. The general chemical formular is $M.n(-SiO_2)_2-Al_2O_3)_n.\ wH_2O)$ where, M is alkali or alkaline earth elements such as K, Na, and Ca, n is 1, 2, and 3 and it represents the degree of condensation. Geopolymer is one type of alumina-silica cements and they produce less $CO_2$and show better mechanical as well as chemical properties including heavy metal stabilization compared to Portland cement. Therefore, they are the most prospecting materials for substituting conventional cement. Geopolymers have a three dimensional network structure such as zeolite and an amorphous phase. The prospecting raw materials for geopolymers are industrial wastes containing large amount of amorphous silica such as fly ash, metakaolin, blast furnace slag etc. and natural silicate materials (Chaung and Chiu 2003).

Geopolymer cement is an innovative material and a real alternative to conventional Portland cement for use in transportation infrastructure, construction and offshore applications. It relies on minimally processed natural materials or industrial byproducts to significantly reduce its carbon footprint, while also being very resistant to many of the durability issues that can plague conventional concretes (Davidovits, J., 1991).

Materials and Methods

Sample Collection

The volcanic mud sample was collected from Yauk Chaung Village, Kyaukphyu Township, Rakhine State and quarry dust samples was collected from Loikaw Township, Kayah State.

Sample Preparation

Volcanic mud was piled up into a cone and dividing it into quarters. Opposite quarters were rejected and the remaining half-portion again treated as before, rolling the sample back and forth on a paper. After quartering, the sample was ground in an agitate motor and pestle and then sieving with 200 mesh sieves.

Quarry dust sample is obtained by crushing the stone boulders of size 100 to 150 mm in the stone crushers. The aggregate is sieved and the sieved aggregates which is less than 4.75 mm in size.

Methods

All chemicals used in this work were the products from British Drug House Chemical Ltd., Poole, England and from Kanto Chemical Co. Inc., Japan, unless otherwise stated. All specific chemicals used are described in detail in each experimental section.

All analytical procedure of the experiment were carried out according to recommended standard text such as Vogel (1964).Various conventional and modern instrumental techniques were used throughout the experimental procedure. These include Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) techniques. Qualitative elemental composition of samples were determined by EDXRF technique. During the experiment, all analytical determinations, instrumental analyses, monitoring of the process systems and the equipment together with the supporting facilities were carried out at Universities ,Research Centre, University of Yangon.

Preparation of Volcanic Mud and Quarry Dust(1:1wt. ratio) Geopolymer and Blended Cement

Volcanic mud and quarry dust in 1:1,1:2 and 2:1 wt. ratios was mixed with 3ml of alkali solution (1:1,1:2,2:1,1:3,3:1) v/v of Na_2SiO_3 :NaOH and 28 % of water were mixed on a non-absorbent base. Immediately the mixture was placed in the plastic mould. After 28 days, the specimens were removed from the plastic mould. The blended cements were prepared by various mixing ratios of prepared GP: commercial cement 1:1,1:2,2:1 w/w.

Table 1: Preparation of Volcanic Mud and Quarry Dust (1:1) based Geopolymer Samples Using Various ratio of NaOH and Na_2SiO_3

GP Sample No	Ratio of Alkali Solutions NaOH : Na_2SiO_3	Concentration of NaOH (M)
A-1	1:1	
A-2	1:2	
A-3	2:1	4
A-4	1:3	
A-5	3:1	
B-1	1:1	
B-2	1:2	
B-3	2:1	8
B-4	1:3	
B-5	3:1	
C-1	1:1	
C-2	1:2	
C-3	2:1	12
C-4	1:3	
C-5	3:1	

Results and Discussions

The result is divided into two parts. The first part is concerned with the physicochemical properties and the characterization of local raw materials volcanic mud and duarry dust**.** The second part is the optimum conditions of sodium hydroxide concentration and sodium silicate for the preparation of volcanic mud and quarry dust based geopolymer.

Physicochemical Properties of Volcanic Mud and Quarry Dust Sample

Moisture content

Moisture content of volcanic mud and quarry dust samples contain 3.7 % and 2.6 % respectively. It is possibly due to basic oxides and those of silicon, iron and aluminium. These oxides are able to absorb moisture. The results are shown in Table 1.

pH

pH values of volcanic mud and quarry dust samples were 11.92 and 9.46 respectively. According to the pH values, the samples were highly alkaline not surprising of the nature of basic oxides. The results are shown in Table 1.

Loss on ignition (LOI)

LOI was essentially a measure of the unburnt carbon in volcanic mud and quarry dust samples. LOI value of volcanic mud was found as 5.3 % and quarry dust as 0.48 %. According to ASTM C 618 guide lines studies, LOI is acceptable for use as a substitute of cement. The results are shown in Table 1.

Specific gravity

The average specific gravity of the volcanic mud and quarry dust were 2.59 and 2.57.They are slightly less than that of Portland Cement (Alpha Cement Brand),thus using volcanic mud and quarry dust samples as a replacement material can reduce the weight of cement. The low specific gravity causes porous, weak and absorptive material and high specific gravity causes good quality of concrete. The results are shown in Table 1.

Fineness

The fineness of volcanic mud and quarry dust depends on the methods of combustion and grinding. The results of fineness of volcanic mud was 27.8 % and quarry dust was 12.9%. The results are shown in Table 1.

Table 1: Physical Properties of Volcanic Mud and Quarry Dust Samples

No.	Sample	Moisture (%)	Loss-on-ignition(%)	pH	Specific gravity	Fineness (%)
1.	Volcanic mud	3.7	5.3	11.92	2.59	27.8
2.	Quarry dust	2.6	0.48	9.46	2.57	12.9

Solubility

The solubility of volcanic mud and quarry dust samples are shown Table 2. According to the experimental results, the samples were slightly soluble in inorganic acids but insoluble in organic solvents. The results are shown in Table 2.

Table 2: Solubility of Volcanic Mud and Quarry Dust Samples

No.	Solvent	Volcanic mud	Quarry dust
1.	Nitric acid	±	±
2.	Sulphuric acid	±	±
3.	Hydrochloric acid	±	±
4.	Acetic acid	-	-
5.	Ethanol	-	-
6.	Methanol	-	-
7.	Sodium hydroxide	-	-
8.	Water	-	-

(+) = soluble (-) = insoluble (±) = slightly soluble

Relative Abundance of the Elements in Volcanic Mud and Quarry Dust Samples by EDXRF method

The relative compositions of the elements in the volcanoic mud and quarry dust samples are shown in Figures 1 and2 and Table 3. According to the experimental results, Si, Ca and Al were found as major constituents and Fe, S and K were found as minor constituents in the volcanic mud sample. In the quarry dust sample, Si and Al were observed as major constituents and Fe, K and Ca as minor constituents.

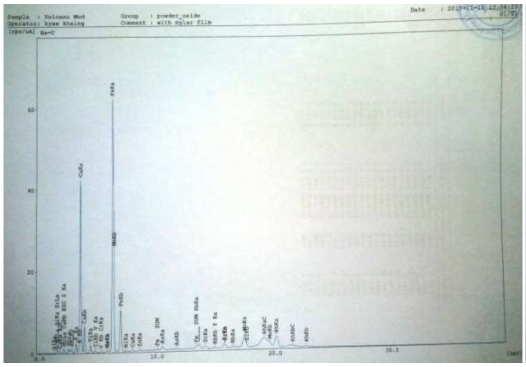

Figure 1. ED XRF spectrum of volcanic mud sample

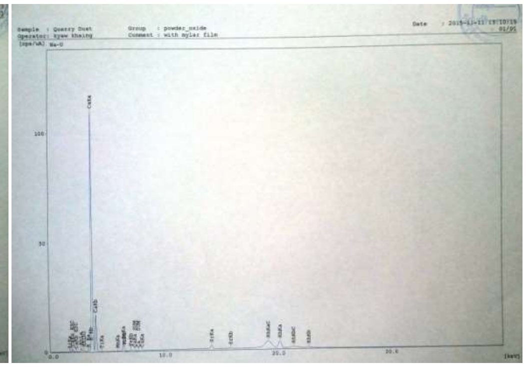

Figure 2. EDXRF spectrum of quarry dust sample

Table 3: Relative Composition of Elements in Volcanic Mud and Quarry Dust Samples

Samples	Relative composition (%)							
	Si	**Ca**	**Al**	**Fe**	**S**	**K**	**Ti**	**Sr**
Volcanic mud	52.06	20.17	16.27	5.10	3.81	1.64	0.64	0.01
Quarry dust	7.74	89.83	-	1.40	-	0.66	0.17	0.12

X Ray Diffractograms of Volcanic Mud and Quarry Dust samples

The X-ray diffractogram of the samples are shown in Figures 3 and 4. It was found to be amorphous form of SiO_2. According to the XRD results, the two samples of the2ϴ value from 28 to 32 which is in indication of crystalline form (Figure 3 and 4). The crystalline form of samples can be used as a Portland cement replacement in concrete.

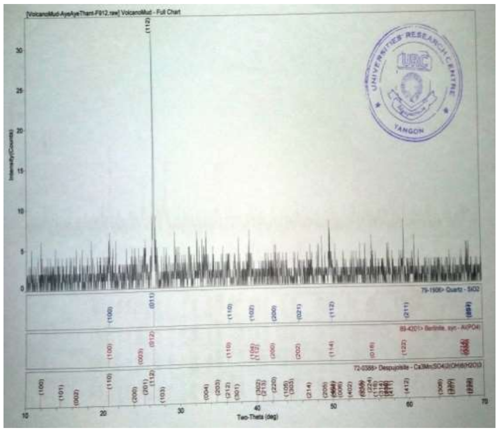

Figure 3. XRD spectrum of volcanic mud sample

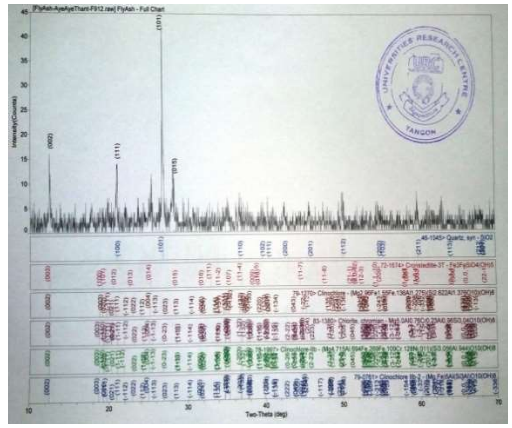

Figure 4. XRD spectrum of quarry dust sample

SEM Micrographs of Volcanic Mud and Quarry Dust Samples

SEM micrographs of volcanic mud and quarry dust samples are shown in Figures 5 and 6**.**Thesefigures showed the diameter of pores that may be approximately 1-10μm range. From the SEM micrographs, the microstructure of quarry dust appeared to be glassy, hollow and porous structure. In the microstructure of volcanic mud sample, the micrograph indicates crystalline nature. It can be considered that the pores are micro-porosity sized particles. It must be note that the cement powder lies in the mixed partial morphological nature of the ingredients.

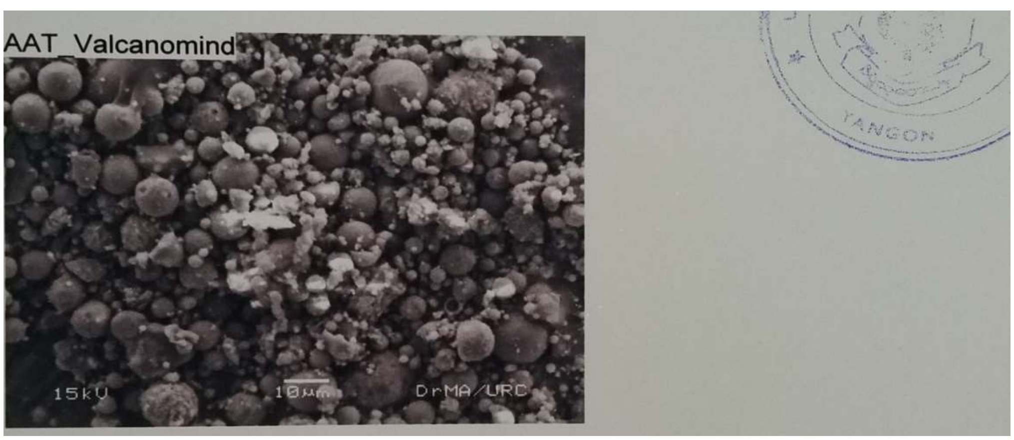

Figure 5: SEM micrograph of volcanic mud sampleat 1000 × magnification

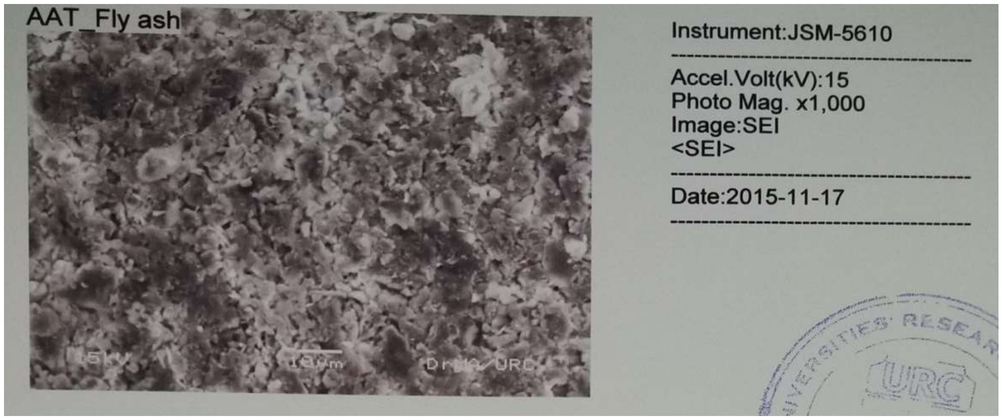

Figure 6: SEM micrograph of quarry dust sample at 1000 × magnification

Pozzolanic Reactivity of Volcanic Mud and Quarry Dust samples

The pozzolanic material of volcanic mud and quarry dust were allowed to react with calcium hydroxide in solution as were as in paste. In case of reaction in solution, volcanic mud and quarry were mixed with saturated solution of calcium hydroxide and definite volume of the solution(filtered) were titrated against standard HCl at different intervals of time. The amount of calcium hydroxide reacted with volcanic mud and quarry dust were determined.

Table 4 and 5 showed that the pozzolanic reactivity of volcanic mud and quarry dust samples. The amount of reacted calcium hydroxide is plotted against time. Figure 7 and 8 showed that the time progressed, the amount of calcium hydroxide reacted were increased. The reactivity was much higher than that at room temperature. The results suggest that volcanic mud and quarry dust are pozzolanic material and its pozzolanic activity increased with the temperature. The pozzolanic reaction can be expressed as:

$$Ca(OH)_2 + SiO_2 \longrightarrow \text{C-S-H (calcium silicate hydrate)}$$

The increase of rate above reaction with temperature may be due to increase of dissociation of $Ca(OH)_2$ in solution giving more Ca^{2+} and OH^- ions. The larger number of ions react with amorphous silica at faster rate.

Table 4: Pozzolanic Reactivity of Volcanic Mud Sample

No. of Experiments	Time(min)	Reacted value of $Ca(OH)_2$ (%)
1	30	48.86
2	60	54.55
3	90	60.23
4	120	64.02
5	150	75.58

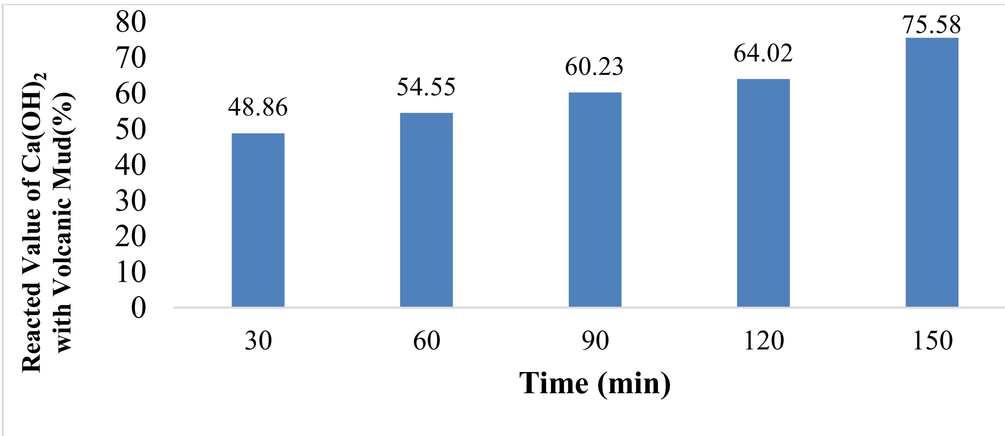

Figure 7: Pozzolanic reactivity of volcanic mud sample

Table 5: Pozzolanic Reactivity of Quarry Dust Sample

No. of Experiments	Time(min)	Reacted value of $Ca(OH)_2$ (%)
1	30	71.59
2	60	75.38
3	90	79.17
4	120	84.85
5	150	88.64

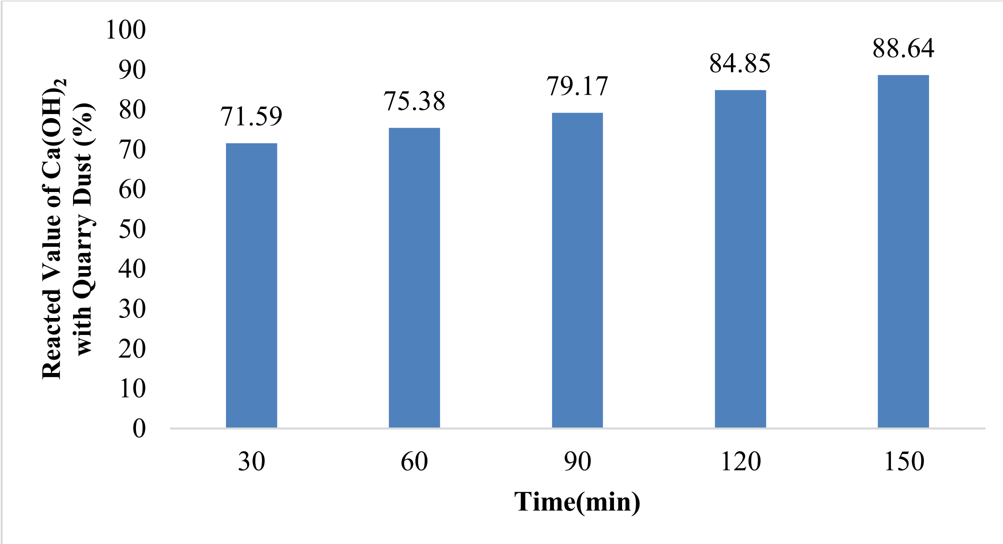

Figure 8: Pozzolanic reactivity of quarry dust sample

The Optimum Condition of Effect of Alkali Concentration on the Prepared Volcanic Mud and Quarry Dust Based Geopolymer

The optimum condition of sodium hydroxide concentration and the ratio of sodium hydroxide and sodium silicate for the preparation ofvolcanic mud and quarry dust based geopolymers were prepared by physical mixing method. Table 6 show that the apparent porosity, water absorption and apparent density of prepared geopolymer samples. In the prepared method, same amount of volcanic mud and quarry dust (1:1) and different volume ratio of (1:1,1:2,2:1,1:3,3:1)of NaOH (4,8,12) M and Na_2SiO_3 were mixed. Table 7 show that the compressive strength of volcanic mud and quarry dust 1:1 based prepared geopolymer at 7,14 and 28 days. The apparent density and compressive strength, (28 days) were found to be maximum when it was prepared with same amount of volcanic mud and quarry dust and (1:3) volume ratio of 12 M NaOH and Na_2SiO_3. Table 8 show that the apparent porosity, water absorption and apparent density of prepared samples (110^{0}C) and the mechanical properties such as compressive strength (28 days)each of sample were measured to assess the quality of volcanic mud and quarry dust based geopolymer.

Table 6: Apparent Porosity, Water Absorption and Apparent Density of Prepared Geopolymer Samples

Concentration of NaOH (M)	GP Sample No.	Apparent Porosity (%)	Water Absorption (%)	Apparent Density (g/ml))
	A-1	15.5	7.58	0.47
	A-2	11.71	8.54	0.56
4	A-3	13.46	6.47	0.79
	A-4	**16.87**	**9.86**	**0.82**
	A-5	11.74	5.48	0.98
	B-1	17.45	9.58	0.91
	B-2	13.79	8.26	0.63
8	B-3	14.54	6.87	0.79
	B-4	**18.91**	**10.54**	**0.91**
	B-5	16.74	7.24	0.63
	C-1	22.68	12.48	0.76
	C-2	17.63	9.53	1.25
12	C-3	22.45	10.54	1.49
	C-4	**23.96**	**13.58**	**1.01**
	C-5	21.57	10.69	1.00

1= 1:1, 2= 1:2, 3=2:1, 4=1:3, 5=3:1($NaOH:Na_2SiO_3$)

Table 7: Compressive Strength of Volcanic Mud and Quarry Dust (1:1) Based Prepared Geopolymer at 7, 14 and 28 days

Concentration of NaOH (M)	Sample No	7 day (N/mm^2)	14 day (N/mm^2)	28days (N/mm^2)
4	A-1	7.45	9.71	13.26
	A-2	8.11	11.28	14.78
	A-3	5.55	7.56	11.47
	A-4	8.25	12.45	16.49
	A-5	7.23	10.23	14.56
8	B-1	9.54	11.74	15.59
	B-2	6.37	10.53	13.42
	B-3	5.44	8.68	12.37
	B-4	12.74	14.56	17.47
	B-5	5.34	7.44	10.54
12	C-1	10.54	12.77	16.12
	C-2	11.71	14.52	17.47
	C-3	12.46	16.12	18.47
	C-4	14.54	16.65	19.85
	C-5	9.68	12.62	17.95

Table 8. Water Absorption, Apparent Porosity, and Apparent Density Prepared Geopolymer Samples (110˚C)

Group	Mix No(V:Q)	Apparent Porosity (%)	Water Absorption (%)	Apparent Density (%)
	1:1	25.30	18.53	1.89
4	1:2	22.01	10.40	1.51
	2:1	25.02	11.60	1.76
	1:1	23.43	16.47	1.73
8	1:2	22.41	10.34	1.41
	2:1	23.35	12.41	1.31
	1:1	30.50	19.30	2.41
12	1:2	24.40	12.80	1.98
	2:1	28.49	14.56	2.20

Mechanical Strength of Volcanic Mud and Quarry Dust Based Geopolymer

Table 9 show that the compressive strength values was found to be high in (1:1weight ratio) at 28 days. Compressive strength values increased as the densities increased. In this research work, the compressive strength was found to be increased as the curing time increased. Table 10 show that the maximum compressive strength of blended cement: commercial cement (1:2)is 35.76 N/mm^{2}at 28 days.

Table 9. Relationship between Time and Compressive Strength of Prepared Geopolymer (GP) in Various Ratio of Volcanic Mud and Quarry Dust

	Compressive Strength (N/mm^2) in different time intervals								
Prepared GP	4M			8M			12M		
Volcanic mud : Quarry dust (weight ratio)	7 days	14 days	28 days	7 days	14 days	28 days	7 days	14 days	28 days
1:1	8.52	11.96	15.41	14.05	17.63	19.36	16.44	18.58	21.41
1:2	6.70	10.74	13.74	11.88	15.91	15.91	13.40	15.27	18.27
2:1	7.9	11.57	14.57	12.18	17.43	17.43	14.05	17.67	20.67

Table 10. Relationship between Time and Compressive Strength of Prepared Blended Cement in Various Ratio and Cement (Alpha Cement Brand)

Blended Cement (BC)	GP: Commercial Cement (weight ratio)	Compressive Strength (N/mm^2) in different time interval		
		7 days	14 days	28 days
BC 1	1:1	21.83	25.45	28.41
BC 2	1:2	28.34	31.71	35.76
BC 3	2:1	23.39	27.89	30.14
Cement (Alpha Cement Brand)	Cement (Alpha Cement Brand)	35.09	40.89	42.61

Conclusion

In this research, volcanic mud and quarry dust were used for the preparation of geopolymer. The determination of physicochemical properties of volcanic mud sample from Kyaukphyu Township and quarry dust sample from Loikaw Township was carried out. From the experimental work, moisture 3.7%, LOI 5.3and pH 11.92,specific gravity 2.59 and fineness 27.8 were found in the volcanic mud sample. In the quarry dust sample, moisture 2.6 %, LOI 0.48 % and pH 9.46,specific gravity 2.57 and fineness12.9 were observed. From the EDXRF and XRD analysis, it was observed that the major oxide composition were present as SiO_2, CaO, Fe_2O_3 and Al_2O_3 in both samples. From the SEM photographs, the microstructure of quarry dust appeared to be glassy, hollow and porous structure. In the microstructure of volcanic mud sample, the micrograph indicates crystalline nature. It can be considered that the pores are micro-porosity sized particles. Same amount of mud volcanic and quarry dust and different ratio (1:1,1:2,2:1) of NaOH (4,8,12) M and Na_2SiO_3 were used as experimental design. The physiochemical test such as apparent porosity, water absorption, apparent density(110˚**C**) and compressive strength (7, 14 and 28 days) of each sample were measured to assess the quality of mud volcanic-quarry dust based geopolymer. Blended cement (GP: cement) and cement(Alpha Cement Brand) of different mixing ratio were carried out at different times. The mechanical strength of the prepared geopolymer (volcanic mud : quarry dust) increases with the higher amount of volcanic mud added but the best ratio was found to be1:1. For the blended cement, pure cement and geopolymer ratio 2:1 was the best.

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