EFFECT OF ALKALI CONCENTRATION ON THE PREPARATION OF RICE HUSK ASH AND KAOLINITE BASED GEOPOLYMER

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Abstract

Geopolymer is a new family of synthetic aluminosilicate materials formed by alkali activation of solidaluminosilicate raw materials. Rice husk ash (RHA) and kaolinite based geopolymer had been prepared from rice husk ash collected from Taungoo Township, Bago region and kaolinite sample from Kyaut Taga, Kyauk Padaung Township, Mandalay Region. The physicochemical properties (moisture content, weight loss on ignition, pH, specific gravity and pozzolanic reactivity) of rice husk ash and kaolinite were determined and these samples were characterized by conventional and modern spectroscopic method (XRD, EDXRF, SEM). Moisture content, weight loss-on-ignition, pH, specific gravity of rice husk ash and kaolinite were found to be 1.9% and 4.6%, 2.6% and 12.3%, 8.8 and 8.3 and 1.87 and 2.82 respectively. The chemical analysis (SiO_2, Al_2O_3, CaO, MgO) was also carried out. It was found that the samples were silica – alumina rich compound. The pozzolanic reactivity of rice husk ash and kaolinite were ranged from 64 % to 94 %. The optimum condition of sodium hydroxide concentration and the ratio of sodium hydroxide and sodium silicate which were used in the preparation of geopolymer have been determined. The physical properties such as apparent porosity, water absorption, apparent density and the mechanical properties such as compressive strength of RHA and kaolinite based geopolymer (GP) were also determined. The apparent porosity and water absorption were ranged from 10.48% to 25.92 % and 5.3% to 16.93 %, respectively. The apparent density values of geopolymer were ranged from 0.52 to 1.89 g/cm^3.The blended cements were prepared by various mixing ratios of GP : commercial cement,(1:1, 2:1,1:2). Compressive strengths of the prepared GP and blended cements at different time intervals have been determined. For all types of cements the maximum compressive strengths were achieved at 28 days after mixing. The optimum ratio of alkali solution was found to be 2:3 volume ratio of 8 M NaOH and Na_2SiO_3.

Keywords: rice husk ash, kaolinite, pozzolanic reactivity, apparent porosity, water absorption, apparent density, compressive strength,

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Introduction

Nowadays, the whole of the construction of concrete structure like industrial building, high way, dams and bridges are developed and standard ingredients are required in making of concrete. Only of the early part of the eighteen century, Portland Cement came to be known.

Myanmar has been producing cement from available raw materials since 1990, but during the all round the development of the 1990 s, the used of cement has increased (Ajay, 2012). Today, the construction work is more expanded and the demand is supplying construction materials increased. So, cost effective local raw materials are needed for cement replacement.(Kyi Kyi San, 2013)

Geopolymer is an amorphous alumino-silicate material. Its structure is silicon and aluminium atoms bonding together by sharing oxygen atoms (Mehta, 1975). Once alumino-silicate powder was mixed with alkaline solution, a paste forms and transforms to hard material and gained strength. Geopolymer belong to the family of inorganic polymers, which are macromolecules linked by covalent bonds principally aluminium and secondarily other metals such as iron (Davidovits, 1999). Geopolymer was applied in many field such as a replacement of Portland cement because its production lower energy and not release the green house gases and use in building and motar application because of their short time strength developments. Geopolymer was prepared by dissolution of raw materials which have silica and alumina such as rice husk ash and kaolinite in alkaline solution.

Rice husk is a by- product of the rice milling industry. It is a unique crop residue with uniform size and high content of ash (14 %-25%)(James, 1986). The silica content of the rice husk ash (RHA) can be as high as 90% - 98%. This husk can be used as a fertilizer in agriculture or as an additive for cement and concrete fabrication(Hunt, 1984). Due to its high silica content, rice husk has become a source for preparation of elementary silica silicon carbide and silicon nitride.

Kaolinite is the principal mineral of the kaolinite group clay minerals (Bogue, 1995). Soil dominated by oxide and kaolinite clays are characterized by very stable soil aggregate and they exhibit a low degree of plasticity. Large amount of oxide and kaolinite clays in a soil contribute to the formation of extremely stable soil aggregrates because the clays tend to neutralize each other. Kaolinite has a net negative charge. Kaolinite directly formed from primary minerals in soils of the humid tropics. Although kaolinite is very stable, it can weather to form gibbsite,$Al(OH)_3$ (Jepson, 2007).

Most commom alkali activator used in geo-polymerization is a combination of NaOH or KOH and Na_2SiO_3 or K_2SiO_3 and play important role in polycondensation process. Addition of Na_2SiO_3 solution as the alkaline activator enhances the reaction between the source materials and the solution. OH^- acts as a catalyst for reactivity, and metal cation serves to form a structural element and balance the negative framework carried by tetrahedral aluminum (Hough, 1956).The addition of activators and increase in concentration results in an increase in volume of small pores and lower total porosity.

The main aim of my research work is to study the effect of alkali concentration on the rice husk ash and kaolinite based geopolymer.

Materials and Methods

Sample Collection

Local rice husk samples collected from Taungoo Township, Bago Region and Kaolinite from Kyauk Pa Daung Township, Mandalay Region (Figures 1 and 2) were used in the present work.

Figure 1: Rice husk ash

Figure 2: Kaolinite

Sample Preparation

Rice husk samples (100 g) were placed in a clean dry porcelain basin and their weight were determined. The sample was placed inside the Electric Muffle Furnace and the temperature was raised gradually from 200°C to 700°C until it was burnt completely. After three hours, the samples were cooled and kept in a dessicator and then weighed again. The percent ash of the sample was calculated.

Kaolinite sample 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 a motar and pestle and then sieving with 200 mesh sieves.

Methods

Moisture content was determined by oven drying method. Measurement of pH was determined byusing pH meter. The specific gravity of samples was determined by the Pycnometer method ASTM (American Society for Testing Materials).Chemical composition of Rice Husk Ash and Kaolinite was determined by using acid digestion of gravimetric analysis method. Pozzolanic reactivity was determined by titrimeric method. Raw materials were characterized by EDXRF, XRD and SEM techniques. Relative abundance of elemental oxide in rice husk ash and kaolinite samples was determined by ED XRF technique using EDX-8000, Shimadzy Co. Ltd, Japan. X-Ray diffraction pattern of the sample was recorded by X-ray diffractometer (Cat – No. 9240 J101, Japan). SEM micrograph of the samples was recorded by Scanning Electron microscope (Model Jeol – JSM – 5610LV, JEOL Ltd).

Preparation of rice husk ash and kaolinite (1:1 wt. ratio) geopolymer and blended cement

Rice husk ash and kaolinite in1:1, 2:1 and 1:2 wt. ratio was mixed with 3mL of alkali solution (1:1, 1:2, 2:1, 3:1, 2:3)v/v of NaOH : Na_2SiO_3 and 28 mL of water were mixed on a non-absorbent base. Alkali solution, NaOH (4,8,12) M and Na_2SiO_3(0.1) M were used. 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 the prepared GP : commercial cement (1:1, 2:1, 1:2) weight ratio.

Table 1: Prepartion of Rice Husk Ash and Kaolinite (1:1 wt. Ratio) Geopolymer Samples Using Various Ratios of NaOH and Na_2SiO_3 Solution

Sample No.	**Alkali Solution NaOH: Na_2SiO_3 (v/v)**	**Concentration of NaOH (M)**
A-1	1:1	
A-2	1:2	
A-3	2:1	4
A-4	3:1	
A-5	2:3	
B-1	1:1	
B-2	1:2	
B-3	2:1	8
B-4	3:1	
B-5	2:3	
C-1	1:1	
C-2	1:2	
C-3	2:1	12
C-4	3:1	
C-5	2:3	

Methods Used for Mechanical Test of Rice Husk Ash and Kaolinite Based Geopolymer

Mechanical properties (compressive strength and tensile strength) of rice husk ash and kaolinite based geopolymer were determined at Civil Engineering Department, YTU. Test specimens (5 cm x 5 cm x 5 cm) cubes were used for testing compressive strength.

Figure 3: Compressive strength test machine

Results and Discussion

The result is divided into two parts. The first part is concerned with the physicochemical properties and the characterization of local raw materials (rice husk ash and kaolinite). The second part is concerned with the optimum conditions of sodium hydroxide concentration and sodium silicate for the preparation of rice husk ash – kaolinite based geopolymer. Before preparation of rice husk ash and kaolinite based geopolymer, some physicochemical properties of these raw material were determined. From this investigation, rice husk ash and kaolinite were more or less soluble in all mineral acid and not soluble at all in organic acid, water, hydroxide solvents (Table 2).

Table 2: Solubility of the Rice Husk Ash and Kaolinite

Solvent	Rice Husk Ash	Kaolinite
Nitric Acid	±	±
Sulphuric Acid	±	±
Hydrochloric Acid	±	±
Acetic Acid	-	-
Ethanol	-	-
Sodium Hydroxide	-	-
Water	-	-

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

Physicochemical properties of rice husk ash and kaolinite

The physicochemical properties such as moisture content, loss-on-ignition, pH and specific gravity in rice husk ash and kaolinite were 1.9% and 4.6%, 2.6% and 12.3 %, 8.8 and 8.3, 1.87 and 2.82, respectively, as shown in (Table 3).The moisture content of the rice husk ash and kaolinite contain 1.9 % and 4.6 %. It is possibly due to basic oxides and those of silicon, iron and aluminium. These are potentially are able to absorb moisture and have the property to become wetted which is one unique property of a cement ingredient. So, the content of moisture in kaolinite was slightly high. Loss on ignition (LOI) was eventually a measure of the un-burnt carbon in rice husk ash and kaolinite. LOI value of kaolinite was relatively high (12.3 %) residual carbon content of the ash. pH value of rice husk ash was 8.8 and kaolinite was 8.3 which is highly alkaline, not surprising of the nature of basic oxide. The inorganic composition of SiO_2, Al_2O_3, CaO, MgO and Fe_2O_3 are present in these samples (Table 4).

Table 3: Physicochemical Properties of Rice Husk Ash and Kaolinite

Samples	Moisture (%)	Loss – on – ignition (%)	pH	Specific Gravity
Rice Husk Ash	1.9	2.6	8.8	1.87
Kaolinite	4.6	12.3	8.3	2.82

Table 4: Relative Abundance of Elemental Oxide by ED XRF Analysis of Rice Husk Ash and Kaolinite Samples

Samples	Relative abundance (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	MnO_2	SO_3	SnO_2	ZnO
Rice husk ash	96.70	-	0.30	0.59	1.73	0.30	0.20	0.37	0.03	0.01
Kaolinite	57.48	23.31	7.13	9.62	1.37	0.76	0.14	-	-	0.01

Characterization of rice husk ash and kaolinite samples

Figures 4 and 5 show the relative composition of the rice husk ash and kaolinite samples. According to ED-XRF pattern, silicon were found to be major in rice husk ash and Kaolinite samples. According to XRD result, kaolinite samples of the 2ϴ value from 28 to 32 which is an indication of crystalline form. For rice husk ask samples, the pyrolysis was carried out in the range 450-700˙C, the silica was predominantly amorphous. (Figure 6 and 7). According to SEM micrograph, small pore and particles with diameter < 10 μm were seen on the surface of both rice husk ash and kaolinite samples (Figure 8).

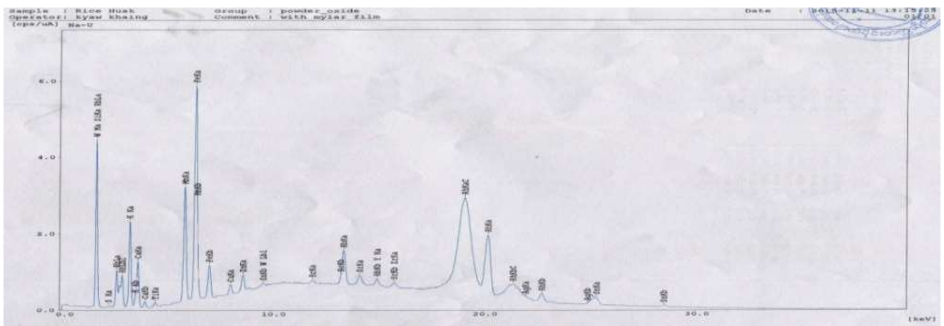

Figure 4: ED XRF spectrum of rice husk ash sample

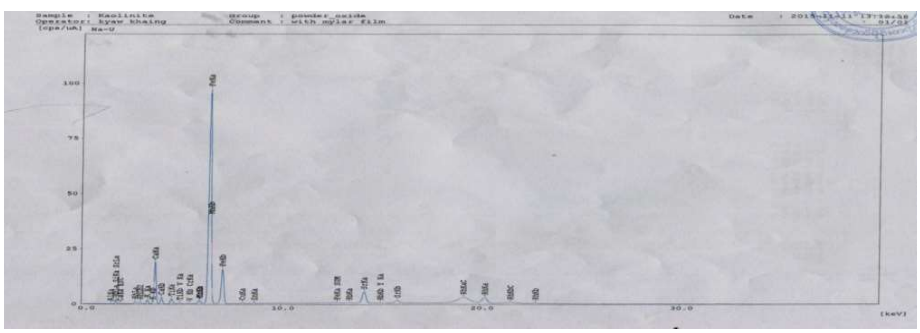

Figure 5: ED XRF spectrum of kaolinite sample

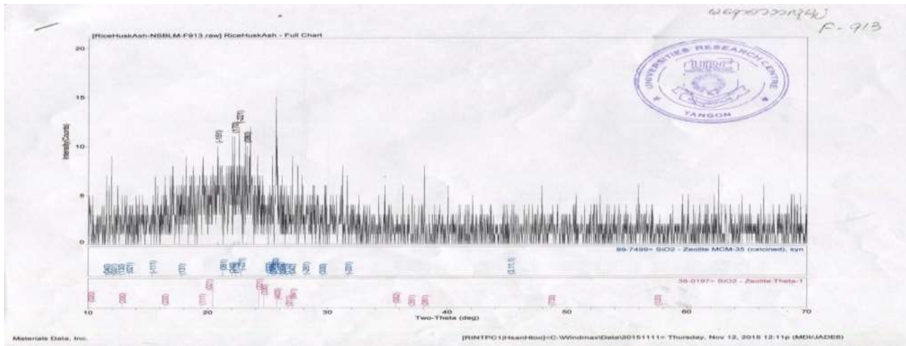

Figure 6: XRD spectrum of Rice Husk Ash sample

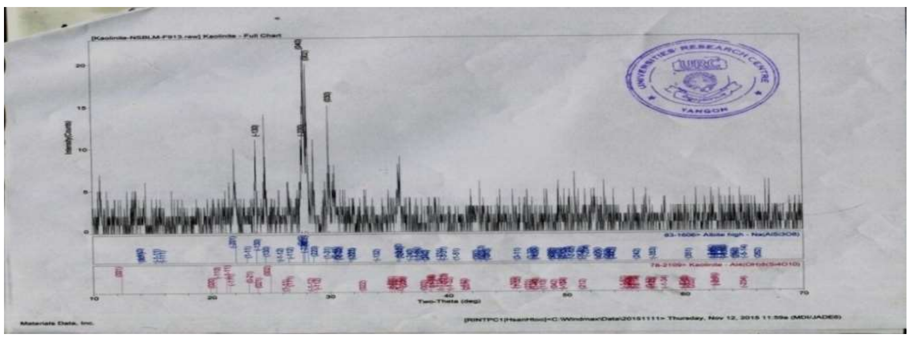

Figure 7: XRD spectrum of kaolinite sample

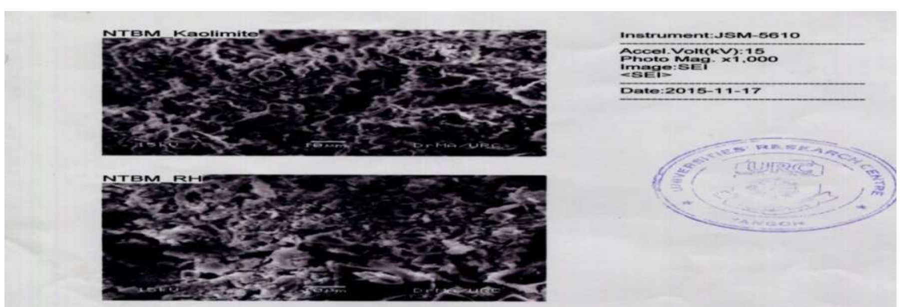

Figure 8: SEM images of rice husk ash and kaolinite samples

Pozzolanic Reactivity of Rice Husk Ash and Kaolinite Samples

In this research work, the pozzolanic reactivity of rice husk ash and kaolinite was found between 64 % to 94 %.These two samples allowed to react with calcium hydroxide nearly to 90 percent and the amount of $Ca(OH)_2$ reacted was increased as the time of reaction increased (Table 5 and 6).

Table 5: Pozzolanic Reactivity of Rice Husk Ash Sample

Experiment	Time (min)	Reacted Value of Ca $(OH)_2$ with Rice Husk Ash
1	30	79.17
2	60	82.96
3	90	86.75
4	120	90.60
5	150	94.40

Table 6: Pozzolanic Reactivity of Kaolinite Sample

Experiment	Time (min)	Reacted Value of Ca $(OH)_2$ with Kaolinite
1	30	64.10
2	60	71.60
3	90	77.28
4	120	82.96
5	150	90.60

The optimum condition of effect of alkali concentration on the prepared rice husk ash and kaolinite based geopolymer

Smaller the pole in prepared geopolymer, it become less permeable to water and lead to more denser. It was found that the less apparent porosity and water absorption percent, the more apparent density values. Sample no. B-5 has the highest value of apparent density, 1.89 g/cm^3 (Table 7).For the apparent density and compressive strength (28 days) were found to be maximum (sample no. B-5). Compressive strength is directly proportional to density value (Table 8).According from these data, the optimum condition for alkaline activator is 2:3. The more the hydroxide content in the ratio the more micro-cracking would be observed. In addition, the more silica content the time become slower. The higher concentration results in higher strength capabilities. However the higher concentration increases the setting and delays polymer formation.

Table 7: Apparent Porosity, Water Absorption and Apparent Density of Prepared Geopolymer Samples (prepared by 1:1 wt. ratio of RHA: kaolinite)

Concentration of NaOH (M)	Sample No.	Apparent Porosity(%)	Water Absorption (%)	Apparent Density (g/cm^3)
4	A-1	12.14	8.72	0.81
	A-2	13.33	9.26	0.73
	A-3	14.12	10.95	0.71
	A-4	26.19	10.42	0.52
	A-5	10.48	5.33	1.21
8	B-1	19.33	10.82	1.72
	B-2	24.16	14.88	1.69
	B-3	24.81	15.48	1.70
	B-4	25.92	16.93	0.81
	B-5	18.52	11.58	1.89
12	C-1	19.93	9.17	1.21
	C-2	17.30	8.55	1.02
	C-3	20.21	10.22	0.93
	C-4	20.01	11.23	0.84
	C-5	18.12	5.11	1.38

Table 8: Compressive Strength of Rice Husk Ash – Kaolinite (1:1 wt. Ratio) Based Prepared Geopolymer Samples (28 days)

concentration of NaOH (M)	**Sample No.**	**Compressive Strength (N/mm^2)**		
		7 days	**14 days**	**28 day**
	A-1	6.01	6.24	12.48
	A-2	4.22	5.12	7.22
4	A-3	5.91	7.23	10.23
	A-4	3.24	3.59	5.61
	A-5	6.58	9.29	15.76
	B-1	8.23	12.11	15.12
	B-2	5.19	7.24	8.58
8	B-3	9.88	13.81	11.21
	B-4	5.25	7.03	6.42
	B-5	10.62	15.17	19.03
	C-1	5.24	5.98	14.12
	C-2	4.05	4.84	11.74
12	C-3	6.25	7.25	10.92
	C-4	3.15	4.06	5.02
	C-5	6.47	12.70	17.14

Table 9: Apparent Porosity, Water Absorption and Apparent Density of Geopolymer Samples Prepared by Different Weight ratio of RHA and Kaolinite

Conc: of NaOH (M)	Mix Ratio of RHA:Kaolinite	Apparent Porosity	Water Absorption	Apparent Density
4	1: 1	16.01	10.91	1.21
	2:1	17.30	12.04	0.34
	1:2	15.91	9.22	1.51
8	1: 1	25.92	16.11	1.89
	2: 1	27.59	18.04	1.53
	1: 2	22.43	15.82	2.33
12	1: 1	20.10	11.21	1.38
	2: 1	23.99	16.39	1.35
	1: 2	19.04	14.60	1.71

Mechanical strength of rice husk ash and kaolinite based geopolymer

The apparent density and compressive strength values is high in (1: 2wt. ratio) of RHA : kaolinite (Table 9).And also, the compressive strength value was found to be high in (1:2 wt. ratio) at 28 days (Table 10). Compressive strength value increased as the densities increased**.** In this research work, the compressive strength was found to be increased as the curing time increased. The maximum compressive strength of blended cement: commercial cement (1: 2) is 29.81 N/mm^2 at 28 days (Table 11).

Table 10: Relationship Between Time and Compressive Strength of Prepared Geopolymer (GP) in Various Ratios of Rice Husk Ash and Kaolinite

Concentration of NaOH (M)	Prepared GP Rice Husk Ash: Kaolinite (Weight Ratio)	Compressive Strength (N/mm^2) in Different Time Intervals		
		7 days	14 days	28 days
	1:1	16.01	10.91	1.21
4	2:1	17.30	12.04	0.34
	1:2	15.91	9.22	1.51
8	1:1	25.92	16.11	1.89
	2:1	27.59	18.04	1.53
	1:2	22.43	15.82	2.33
12	1:1	20.10	11.21	1.38
	2:1	23.99	16.39	1.35
	1:2	6.72	12.60	18.81

Table 11: Relationship between Time and Compressive Strength of Blended Cement and Commercial Cement (Elephant Brand)

Blended Cement : Commercial Cement (weight Ratio)	Compressive Strength (N/mm^2) in Different Time Intervals		
	7 days	14 days	28 days
1:1	17.64	21.50	23.94
2:1	9.21	15.72	19.32
1:2	22.24	25.65	29.81
Cement (Elephant Brand)	31.41	36.14	40.77

Conclusion

The physicochemical properties of rice husk ash and kaolinite were determined by conventional and modern instrumental techniques. The physical properties such as moisture content and loss-on-ignition in rice husk ash and kaolinite were respectively to be found that 1.9 % and 4.6 %,2.6 % and 12.3 %. pH and specific gravity in rice husk ash and kaolinite are 8.8 and 8.3. and 1.87 and 2.82, respectively. Rice husk ash and kaolinite have good pozzolanic properties which react with calcium hydroxide forming calcium silica hydrate. Pozzolanic reactivity of these sample increase with increase of reaction time. The optimum ratio of alkaline activator is 2:3 v/v sodium hydroxide and sodium siicate. The optimum concentration of sodium hydroxide concentration is 8M.Investigation about rice husk ash and kaolinite based geopolymer have found a potential material for replacing the use of Portland cement in infrastructure development thus decrease the carbon dioxide emission. However the different samples may give different reactivities due to their varying chemical compositions. The influence of NaOH molarity and alkaline activator ratioare essential for achieving the optimum strength of geopolymer. The use of rice husk ash and kaolinite as geopolymer are more environmentally friendly and cost compared to ordinay Portland cement.

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