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Utilization of Red Mud and Rice Husk Ash for Synthesizing Lightweight Heat Resistant Geopolymer–Based Materials

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ABSTRACT:*Geopolymer is an inorganic polymer composite developed by Joseph Davidovits in 1970s. Such material has potentials to replace Ordinary Portland Cement (OPC)-based materials in the future because of its lower energy consumption, minimal CO_2 emissions and lower production cost as it utilizes industrial waste resources. Hence, geopolymerization and the process to produce geopolymers for various applications like building materials can be considered as green industry. Moreover, in this study, red mud and rice husk ash were used as raw materials for geopolymeric production, which are aluminum industrial and agricultural wastes that need to be managed to reduce their negative impact to the environment. The red mud and rice husk ash were mixed with sodium silicate (water glass) solution to form geopolymer paste. The geopolymer paste was filled into 5-cm cube molds according to ASTM C109/C109M 99, and then cured at room temperature for 28 days. These processes are to make sure the geopolymerization reaction happened inside the volume. These products were then tested for compressive strength and volumetric weight. Results indicated that the material can be considered lightweight with a compressive strength at 28 days that are in the range of 5.86 to 25.45 MPa. Moreover, the geopolymer specimens were also tested for heat resistance at a temperature of 1000^{o}C for 2 hours. Results suggest high heat resistance with an increase of compressive strength from 36% to 166% after exposed at high temperature. The properties of raw materials and geopolymer products were also determined by analytical techniques that included chemical composition by X Ray Flourescence (XRF), mineral composition by X Ray Diffraction (XRD).*

KEYWORDS –*Geopolymer,Green Industry, Red Mud, Rice Husk Ash,Waste Management*.

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I. INTRODUCTION

Geopolymer, as coined by Davidovits [1], is an inorganic polymer composite which has a potential sustainable construction material because of its lower energy and carbon footprint as compared to Portland cement-based materials [2-6]. Such material uses industrial waste such as red mud, coal fly ash, coal bottom ash, blast furnace slag, and others as raw material which reduced its cost of production [1, 2, 4, 7, 8]. These raw materials contain high silica and alumina resources in amorphous or semi-crystal phases that are consistent with geopolymerization reactions in high alkaline condition. The alkaline activators are known as sodium silicate (Na_2SiO_3), sodium hydroxide (NaOH), potassium silicate (K_2SiO_3), potassium hydroxide (KOH), and others. Geopolymer-based materials are synthesised in many methods depends on the cured regime such as at room temperature, high pressure, high temperature, and in steam condition [1, 8, 9].

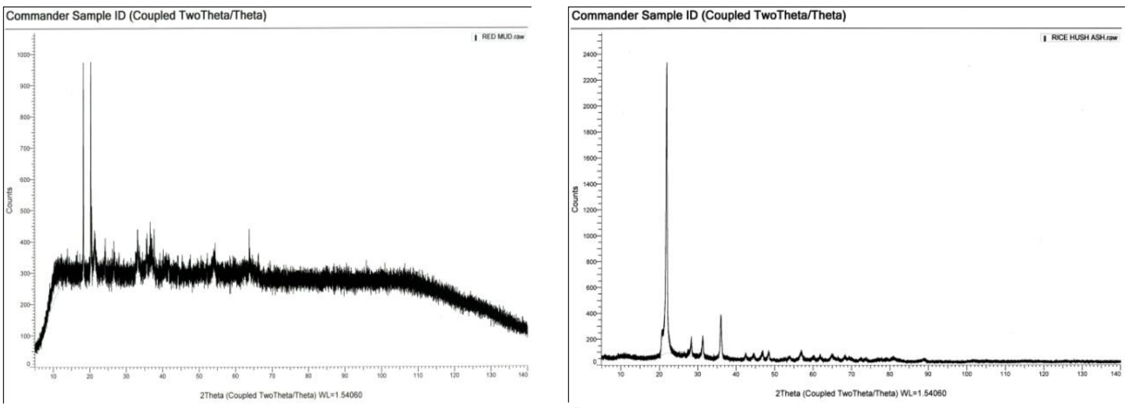
Red mud (RM) is the waste generated during aluminum production from bauxite ore. It depends on the quality of bauxite mine which could affect the output of aluminum production. To produce 1 tonne of metallic aluminum, this Bayer process generates from 0.6 – 2.5 tonnes of red mud [2-4,10-11]. Globally, it is estimated that there has been over 70 million tonnes of this red mud (RM) waste being discharged every year [10-12]. RM waste is fine powder and thus easy to disperse into the surrounding environment which may lead to ecological problems. Currently, RM is contained in dams but these use up a lot of land area. Moreover, these dams pose risk to surrounding residential areas. In fact, in 2010, an accident wherein the failure of red mud dam occurred in Hungary caused serious environmental consequences and health impact to people [10, 13-14]. Therefore, it is imperative to manage these red mud wastes properly to reduce its impact to environment and community. For chemical composition, RM has high alumina (Al_2O_3 or $Al(OH)_3$) and this is one of advantages to utilize RM as a raw material supplying aluminum or aluminate resource for the geopolymer production [3, 6, 10-13].

Rice husk ash (RHA) is high–silica material made from burning rice husk. Rice husk takes up about 20% weight of rice and its compositions include 15 – 20% SiO_2, the others are cellulose and lignin [2-4, 10-12, 15-16]. After the burning process, total weight of obtained RHA is about 20% weight of rice husk. This characteristic mainly depends on burning conditions such as temperature, holding time, among others. Therefore, RHA has high amount of amorphous or activated silica (SiO_2) which is over 85% (in weight). RHA supplies high quality silica resource applied in many fields of industry such as plastics, rubbers, steels, building materials, and others. In 2011, rice production were over 700 million metric tons globally, wherein more than 90% came from Asean countries such as China, India, Indonesia, Bangladesh, Vietnam, Burma, Thailand, and the Philippine. Hence, the total estimated RHA reserves are over 28 million metric tons every year [2-5, 17-18].

There have been many problems existing in Viet Nam as well as developing countries for management of the solid waste. The researchers are finding good solutions for treatment and reuse the solid waste as raw materials for other industries. This study would like to supply a useful solution for utilization of red mud and rice husk ash to produce lightweight heat resistant geopolymer-based materials which can be compared and replaced for building materials such as OPC-based materials.

II. MATERIALS AND METHODS

In this research, both red mud and rice husk ash from Vietnam were used to produce the geopolymer mixture. They are the raw materials in geopolymerization reactions to create the mechanical strength for product. RM waste came from Tan Rai Bauxite Plant, Lam Dong Province, Vietnam was dried at 110^{o}C for 24 hours, ground using ball miller for 30 minutes, and then passed 90µm-siever to obtain the raw material in powder. On the other hand, rice husks from Mekong delta, South of Viet Nam were burned at 700^{o}C for 1 hour at Laboratory of Ceramic Materials to obtain rice husk ash. RHA was ground using ball miller for 30 minutes, and then passed 90µm-siever to obtain the raw material in powder. All of the raw materials were characterized for chemical and mineral compositions using XRF and XRD, respectively. In which, RM contains high alumina (18.98%) in amorphous or semi-crystalline structure and RHA contains high amorphous silica (90.9%) summarized in **Table 1**. As shown from the XRD patterns of RM and RHA, evidence of amorphous silica and alumina was observed as described by the noise at the bottom hump of the XRD spectrums (see Figure 1). There also have been some sharp peaks associated with crystalline minerals of gibbsite ($Al_2O_3.3H_2O$) at 18^o - 2Theta angle and iron oxide (Fe_2O_3) at 20^o - 2Theta angle in XRD pattern of RM (**Fig. 1a**) and cristobalite (SiO_2) in XRD spectrum of RHA (**Fig. 1b**). Note that the amorphous compositions are necessary conditions to conduct geopolymerization for RM based geopolymer materials. Thus, RM and RHA serve as the reactants in the geopolymerization process.



(**a**) (**b**)

Fig. 1: XRD patterns of red mud (a) and rice husk ash (b)

Table 1. Chemical composition (wt.%) of red mud and rice husk ash from Viet Nam.

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	Others	L.O.I [1]
RM	4.25	18.98	49.90	0.87	2.06	0.05	5.62	1.48	16.52
RHA	90.90	1.12	0.54	1.41	ND[2]	4.66	ND[2]	0.06	0.77

[1] L.O.I = Loss On Ignition.
[2] ND = Not Detected.

Water glass solution (WGS) was used as an alkaline activator to increase pH value and supply the sodium hydroxide reactant for the geopolymer mixtures. The sodium silicate solutions have lower pH value (12-13.5) than the alkali hydroxides but an amount of silicate oligomer precursor in alkali silicate solutions will rapidly dissolve and react the solid alumino-silicate resources (Al_2O_3 and SiO_2) in the geopolymer mixtures [1, 8, 19]. The reactant was a product of Bien Hoa Chemical Factory, Viet Nam, it has silica modulus (SiO_2:Na_2O ratio) at 2.8:1 and was dissolved to obtain 50%-water solution.

Table 2 summarizes the mix proportions used in this experiment. The schematic diagram of the experimental process is shown in Figure 2. RM, after being dried at 110°C for 24 hours (VENTICELL DRIER), was ground in 30 minutes (BALL MILLER of Ceramic Instrument) and then passed through 90µm- mesh (siever, Retsch AS-200 Seive Shaker). Rice husk was burned at 700°C for one hour (NABERTHERM), and then also ground in 30 minutes and passed through 90µm-mesh to obtain the RHA powder. All raw materials were mixed for 20 minutes with 10% to 30% water glass solution (Lab cement mixer) and water was added to get a pH value around 12 to get geopolymer mixtures in paste. The pastes were molded in 50x50x50mm cube-cement molds and cured at room temperature (28°C, 80% humidity) for 28 days followed with ASTM C109/109M [20]. The 28-day geopolymer specimens were tested for compressive strength, volumetric weight, and heat resistance. Then, the geopolymer specimen with the highest value of compressive strength was characterized microstructure using XRD.

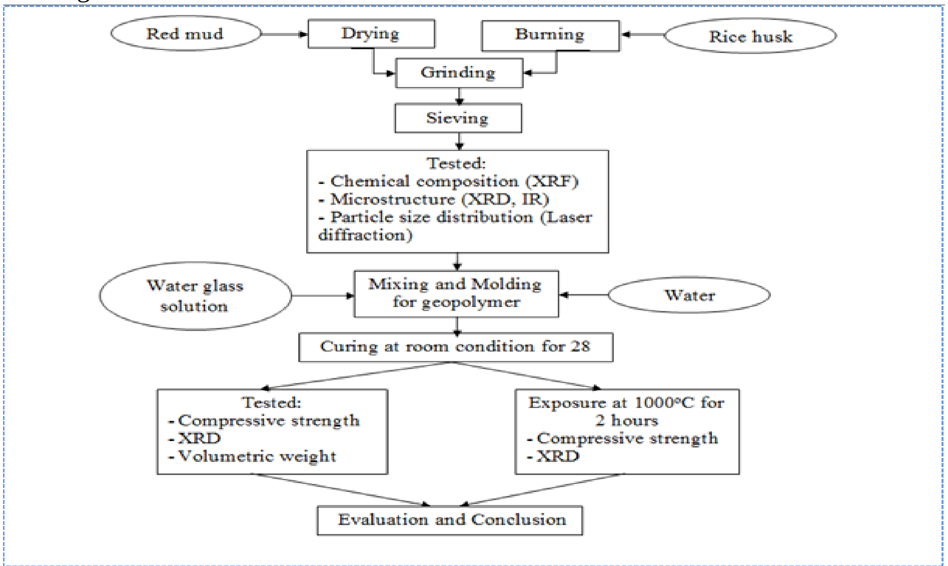


Fig. 2: The experimental process to produce geopolymer-based materials from RM and RHA

Table 2. Mix proportions of raw materials (wt.%) for preparation of geopolymer production.

Sample Name	RM	RHA	WGS
A1	22.5	67.5	10
A2	45.0	45.0	10
A3	67.5	22.5	10
B1	20.0	60.0	20
B2	40.0	40.0	20
B3	60.0	20.0	20
C1	17.5	52.5	30
C2	35.0	35.0	30
C3	52.5	17.5	30

III. Results And Discussion

3.1. Compressive strength (MPa) and volumetric weight (kg/m^3)

Table 3. Properties of geopolymer produced from red mud and rice husk ash.

Sample	**Volumetric Weight (kg/m^3)**	**Compressive Strenghth (MPa)**		**Change of Compressive Strength (%)**
		Room condition	After exposed at 1000°C	
A1	1259	9.24	16.39	77.38
A2	1469	7.43	14.78	98.92
A3	1621	5.86	11.46	95.56
B1	1270	25.45	67.83	166.52
B2	1460	18.22	40.24	120.86
B3	1590	16.43	36.27	120.75
C1	1205	22.36	30.57	36.72
C2	1425	17.35	28.56	64.61
C3	1537	14.68	25.39	72.96

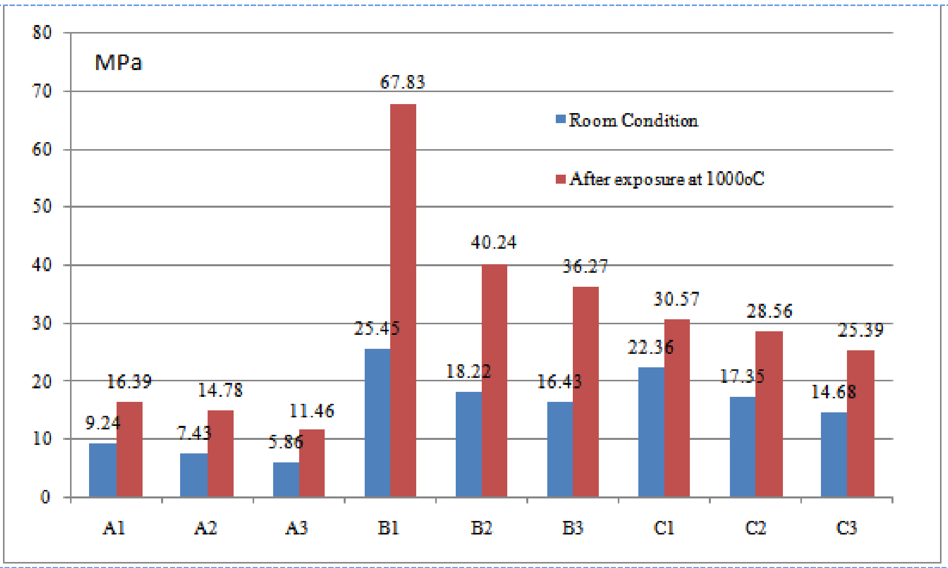


Fig. 3: Compressive strength of geopolymer before and after exposed at 1000°C

Table 4. Requirements for upper limits of compressive strength (MPa) for lightweight concrete brick after cured at 28 days in ASTM C55 and C90 [21-22].

Compressive Strength (min, MPa) after 28 days for lightweight concrete brick (ASTM C55)		**Compressive Strength (min, MPa) after 28 days for load-bearing concrete masonry units (ASTM C90)**	
Average of 3 Units	Individual Unit	Average of 3 Units	Individual Unit
13.1	11.7	24.1	20.7

Volumetric weight is a parameter evaluated by mass per volume (kg/m^3) in the same sample. In this study, the cubic samples are determined as in standard of ASTM C109/C109M for the weight and volume values [20]. The volumetric weight of geopolymer specimens were found to be from 1205 to 1621 kg/m^3 (Table 3). This means that the geopolymer-based materials belong to lightweight material group classified by ASTM C55 and C90 for concrete brick [21-22]. The higher the proportion of rice husk ash is, the lower this property is, because rice husk ash is a lightweight material that contains high silica in its composition [1, 8]. It is noted that the lightweight materials are preferred for high-rise buildings and applied for insulation for sound and heat resistance.

3.1. Heat Resistance

All geopolymer samples were tested for heat resistance by keeping the specimen at a furnace at the temperature at 1000°C for 2 hours, with a heating rate at 5°C/min and a natural cooling process to room temperature. After exposure with this high temperature, the samples were tested for compressive strength. Heat resistance of geopolymer-based material was evaluated by percentage change (%) of compressive strength before and after geopolymer specimens were exposed at 1000°C. This procedure is similar to test done by Kong et al., (2007) [23] and Pan et al., (2012) [24]. Results indicate that the compressive strength significantly increased from 36% to 166% as shown in Figure 3 and summarized in Table 3. Because the geopolymerization reactions created alumino-silicate network chains that sustains at high temperatures. This could be also due to sintering that may be occurred at high temperature in geopolymer samples, similar to what is happening in ceramic process [23 -24].

In general, the geopolymer-based materials had good engineering properties and can be used as a lightweight material. More specially, the products with high heat resistance (at least 1000°C) can work at high temperature as insulation.

3.1. Microstructure of Lightweight Heat Resistant Geopolymer-based Materials

Geopolymer sample A with the highest compressive strength and heat resistance was chosen for microstructure characterization using XRD (X-ray diffraction) (see Figure 4). In which, the XRD analysis is used to determine crystals of raw materials and geopolymeric products. Differences for microstructure, mineral compositions between raw materials and products are obviously shown through the XRD patterns. These are various peaks for diffractive intension, position of 2θ angles, and width of the peaks. Therefore, the XRD analysis helps this study assess the quality of used raw materials as well as efficiency of reactions in comparison with initial proposed objectives [25].

The XRD pattern shown that main compositions in the crystalline structure of geopolymer-based materials are silicon oxide (at 22^o - 2Theta angle) and some minerals such as sodium aluminum silicate (at 21.5^o - 2Theta angle), iron silicon oxide (36^o - 2Theta angle). Two peaks of gibbsite and iron oxide at 18^o - 2Theta angle and 20^o - 2Theta angle, respectively are typically associated with red mud raw material (**Fig. 1a**) disappeared in this XRD spectrum because there was reaction of geopolymerization among reactants resulting to an increase of mechanical strength of geopolymer specimens. Moreover, there is no peak of any zeolite crystal in the geopolymer-base material since this study only considered curing at room temperature. Note that zeolite-like structure would most likely form at higher temperature condition, for example, over 50^{o}C in hydrothermal condition [26-29]. Amorphous phase in its microstructure has also been observed with noise and broadening of the XRD spectrum background.

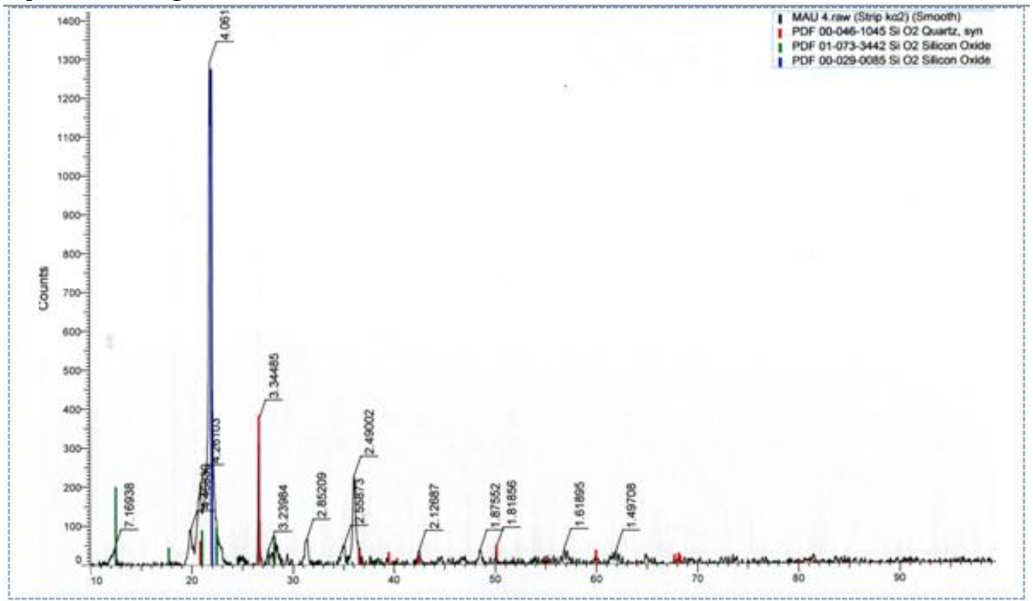


Fig. 4: XRD pattern of geopolymer –based materials, sample B1.

IV. CONCLUSION

Red mud is an industrial waste that can effect negatively the environment if not properly managed. It is necessary to have more research in utilizing this as raw materials for other applications. In this research, red mud in combination with rice husk ash in high alkaline condition can be geopolymerized to form products that can be compared with lightweight concrete brick in ASTM C55 and C90 in terms of mechanical strength and volumetric weight. More specially, the geopolymer products have high compressive strength even if exposed at high temperature (1000^{o}C). That can be evaluated as heat-resistant materials. This investigation also described the microstructural properties with the aid of XRD analysis. In which, the geopolymer-based material contains crystal structures of silicon oxide, sodium aluminum silicate, and ion silicate oxides. Future work will be done to characterize further the microstructure and optimize the properties for a lightweight heat-resistant geopolymer material.

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