EFFECT OF KARANGNUNGGAL BENTONITE ADDITION ON THE MECHANICAL STRENGTH OF CONVENTIONAL CERAMICS

PENGARUH PENAMBAHAN BENTONIT KARANGNUNGGAL TERHADAP KEKUATAN MEKANIK KERAMIK KONVENSIONAL

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ABSTRACT

Bentonite can be used as an additive in ceramics production. It can increase the thermal resistance and flexural strength of ceramics. Indonesia has a large amount of bentonite deposit. One of them is located in Karangnunggal, Tasikmalaya. The aim of this research is to study the effect of bentonite to increase the flexural strength of ceramic. The raw materials consisting of kaolin, feldspar, and quartz were used as raw materials in ceramics production. The weight percents of kaolin and quartz were fixed at 55 % and 20 %, whereas weight percents of feldspar and bentonite were varied at 25 %, 20 %, 15 %, 10 % and 0,5 %, 10 %, 15 %. The firing temperature was kept at 1,200 °C. Result of the experiment shows that the best composition to achieve the highest dry flexural strength at 254.70 kg/cm^2 is at 55 % kaolin, 20 % quartz, 15 % feldspar, and 10 % bentonite.

Keywords: bentonite, additive, ceramics, flexural

ABSTRAK

Bentonit dapat digunakan sebagai bahan aditif dalam produksi keramik. Material ini dapat meningkatkan ketahanan panas dan kekuatan lentur keramik. Indonesia memiliki deposit bentonit dalam jumlah besar, Salah satunya terletak di Karangnunggal, Kabupaten Tasikmalaya. Tujuan penelitian ini adalah mempelajari pengaruh bentonit untuk meningkatkan kekuatan lentur keramik. Bahan baku yang terdiri dari kaolin, felspar, dan kuarsa digunakan sebagai bahan baku dalam produksi keramik. Persen berat kaolin dan kuarsa ditetapkan sebesar 55 % dan 20 %, sedangkan % berat felspar dan bentonit masing-masing divariasikan sebesar 25 %, 20 %, 15 %, 10 % dan 0,5 %, 10 %, 15 %. Pembakaran dilakukan pada temperatur 1.200 °C. Hasil penelitian menunjukkan bahwa komposisi terbaik untuk mencapai kekuatan lentur bakar tertinggi pada 254,70 kg/cm^2 adalah 55 % kaolin, 20 % kuarsa, 15 % felspar, dan 10 % bentonit.

Kata kunci: bentonit, aditif, keramik, lentur

INTRODUCTION

Bentonite is classified as a hydrated clay in the colloid form. It mainly consists of montmorillonite $(Al_2, Mg_3) (Si_4O_{10}) (OH)_2 \cdot nH_2O$, which is the layer of $(SiO_4)^{2+}$ tissues with its ratio of Si/O is equal to 2/5, (Rowe, Sheskey and Quinn, 2009). Besides montmorillonite, the bentonite also consists of other minerals such as illite $\{(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2,(H_2O)\}$, kaolinite $\{Al_2Si_2O_5(OH)_4\}$, halloysite $\{Al_2Si_2O_5(OH]_4\}$, quartz (SiO_2), calcite $(CaCO_3)$, and pyrite (FeS_2) (Liu, Xie and Qin, 2017). In general, bentonite deposits are formed through rock weathering, reactions between rock with acidic hydrothermal

solution, volcanic dust devitrification, and sedimentation from tufa deposition containing silica.

Two types of bentonite are known as sodium (sodic) bentonite and calcium (calcic) bentonite (Savic-Gajic et al., 2014; Boussak, Chemani and Aicha, 2015). The sodium bentonite contains more Na^+ ion than Ca^{2+} and Mg^{2+} ions. Expand bentonite in the water increases its viscosity. Potassium bentonite, which contains more potassium and magnesium (in the form of K_2O and MgO, respectively) absorbs less water so that it does not form a suspension.

Bentonite has been used in various sectors such as construction, environmental protection, electronic industry, agriculture, food processing, textile industry, soap production, biomedics, etc. (Savic et al., 2012, 2014; Boussak, Chemani and Aicha, 2015). In the ceramic industry, bentonite is usually mixed with another tuff such as clay, feldspar, and quartz to produce tiles, sanitary, tableware and decorative ceramics (Hosten and Cimilli, 2009). Composition of the soft ceramic is usually 25% of clay, 25% silica, and 50% sodium feldspar, whereas the composition of hard ceramic is 50% of clay, 25% silica and 25% potassium feldspar (Gualtieri, 2007; Boussak, Chemani and Aicha, 2015). Bentonite, clay, and silica are also often used as an additive reagent, binder, and filler (Djambazov, Yoleva and Malinov, 2009). Mixing and firing of those minerals at high temperature result in mullite formation, whereas the firing pure clay at 1000 °C results in a better mullitization process. On the other hand, clay firing of clay that contains mullite impurities can only be formed at a temperature above 1200 °C. (Septawendar, Nuryanto and Subari, 2007; Boussak, Chemani and Aicha, 2015).

The aim of this research is to evaluate the potential application of bentonite from Karangnunggal as an additive reagent to increase flexibility and pressure strength of the ceramics. The evaluation includes the analyses of mineral composition and chemical/physical property (dry shrinkage, firing shrinkage, dry flexural strength, thermal flexure, and water absorption).

METHODOLOGY

Research activities consist of sampling the bentonite, kaolin, feldspar, and quartz, whereas laboratory activities consist of bentonite characterization, ceramics preparing and product testing.

The minerals used in the experiment were bentonite, kaolin, feldspar, and quartz. Those were sampled from different locations in Indonesia. Bentonite, kaolin, and feldspar were obtained from Tasikmalaya, whereas quartz was taken from Sukabumi. The exact location of bentonite used in this study was Santrijaya Village, District of Karangnunggal, Tasikmalaya Regency, West Java Province (S = 07° 36' 54.3'' / E = 108° 07' 02.9"). The picture of the location is shown in Figure 1. The morphology of bentonite deposit was like a grayish white smooth lens. The bentonite was formed from breccia tuff. This tuff underwent alteration that leads to the diagenesis reaction to form bentonite (Figure 2).

The minerals were dried in an oven at 100 ^{o}C for 2 hours to reduce its moisture of the minerals. The dried minerals were ground and milled to attain a particle size of 150 mesh (100 microns). In order to reveal the additive property of the pure bentonite, the ground and milled bentonite were shaped and pressed to form a specimen with the size of 12 cm x 1.5 cm x 1 cm, before being heated at 1,200 °C for 6 hours. The heated specimen was subjected to measurement of weight loss, stiffness, thermal stiffness, and the ability to absorb water. The composition of raw materials, which is based on the previous work by Boussak, Chemani and Aicha (2015), is shown in Table 1.

Meanwhile, other samples that consisted of bentonite and kaolin was milled in the pot mill for 6 hours, whereas feldspar and quartz were milled for 10 hours. The milled minerals were mixed, shaped and pressed to produce a specimen. The size of the specimen is 12 cm $\times$ 1.5 cm $\times$ 1 cm. After being pressed, the specimen was dried at room temperature for seven days prior to firing at 1,200 °C. The mechanical strength of the fired specimen was analyzed to reveal its mechanical strength and water absorption capacity. The flow sheet of ceramics preparation is shown in Figure 3.

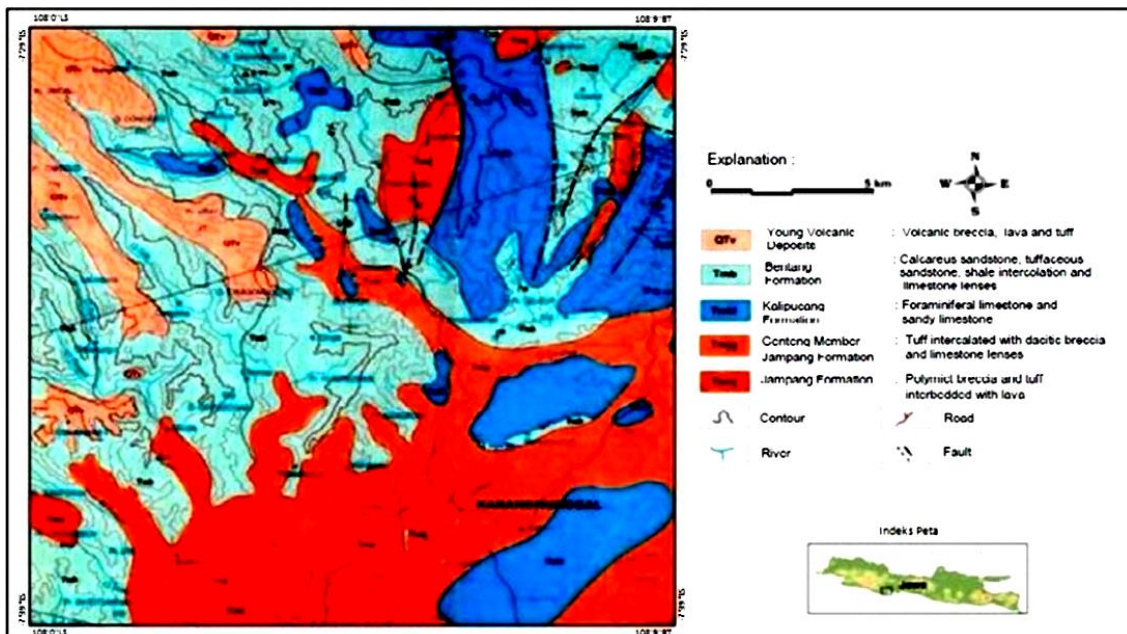Figure 1. Bentonite deposit in Karangnunggal

Figure 2. Geological map of Karangnunggal and surrounding area (Supriatna *et al.*, 1992)

Table 1.   Composition of ceramics

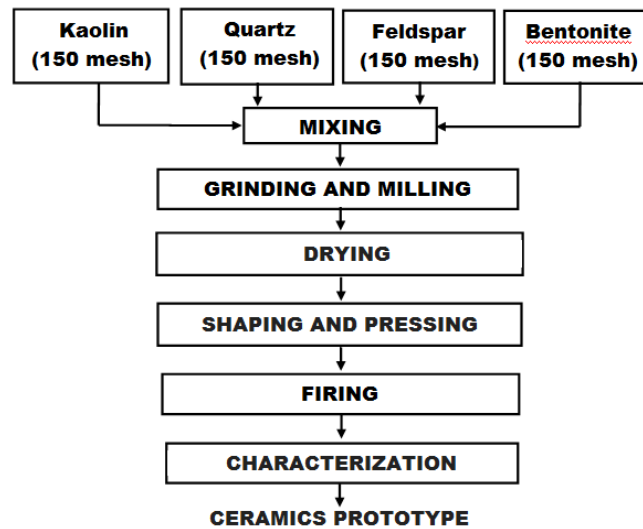| Minerals	% Weight			
	BC-0	BC-1	BC-2	BC-3
Bentonite	0	5	10	15
Kaolin	55	55	55	55
Silica sand	20	20	20	20
Feldspar	25	20	15	10

Figure 3. Flowsheet of ceramics prototype preparation

During the firing process, the dehydroxylation of kaolinite took place at 450 °C. Then in the firing process up to 1,200 °C, a reaction occurred between feldspar and quartz/silica and the formatted of mullite, respectively. The formatted of mullite contributed to the significant increase of the mechanical strength of the ceramics (Boch and Niepce, 2007).

The petrographic analysis was conducted through an optical microscope (Nikon Ipol-50) to observe the mineral composition of the bentonite. Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy (SEM-EDX, Rigaku Japan) was applied to observe the bentonite morphology and to identify the minerals within the Karangnunggal bentonite. The exact minerals that composes bentonite were confirmed through XRD analysis (Shimazu, Japan). Chemical analysis was carried out on the raw materials using wet analysis method. The mineral was dissolved in aqua regia and the content of Al_2O_3, Fe_2O_3, CaO, TiO_2, and MgO in the resulted solution was analyzed using Atomic Absorption Spectroscopy (AAS, Shimazu, Japan). Meanwhile, the content of SiO_2, Na_2O/K_2O_2 was analyzed through gravimetric method and flame photometer, respectively.

RESULTS AND DISCUSSION

Petrographic Analysis

Based on the petrographic analysis bentonite sample from Karangnunggal consists of an altered fragment of silica, mica, and montmorillonite in the matrix of volcanic glass. The texture of the sample is clastic with size in the range of 0.06-0.5 mm. The sample is composed of 38 % quartz, 46 % montmorillonite, 13 % halloysite, 2 % volcanic glass, and 1 % mica. The transformed mineral in which feldspar, quartz, and hornblende are interpreted as riolitic/dasitic, is shown in Figure 4.

Morphology Analysis

Based on morphology and composition analysis through Scanning Electron Microscope (SEM) at a magnification of 500 times, shown in Figure 5 the bentonite sample from Karangnunggal is dominated by montmorillonite. The figure shows that the morphology of Karangnunggal bentonite is afan-shape, whereas halloysite is in the fine grain. The Karangnunggal bentonite was formed from tuff/ feldspathic through a hydrothermal process to form montmorillonite and halloysite minerals.
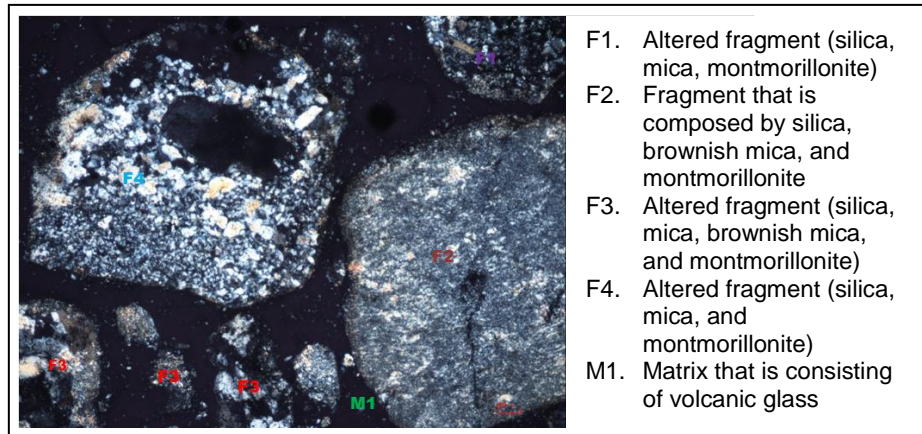
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F1.	Altered fragment (silica, mica, montmorillonite)
F2.	Fragment that is composed by silica, brownish mica, and montmorillonite
F3.	Altered fragment (silica, mica, brownish mica, and montmorillonite)
F4.	Altered fragment (silica, mica, and montmorillonite)
M1.	Matrix that is consisting of volcanic glass

Figure 4. Petrographic analysis of bentonite sample from Karangnunggal
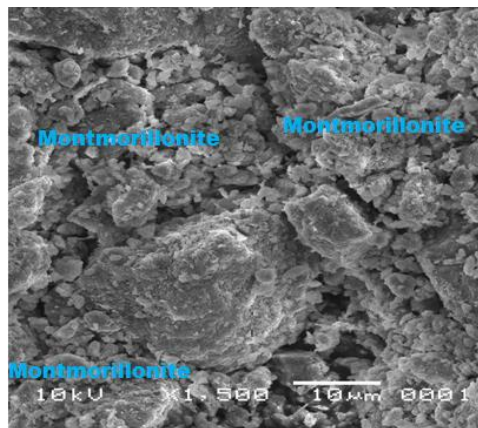
Figure 5. Morphology and compositional analysis of bentonite sample from Karangnunggal

X-Ray Diffraction Analysis

Result of XRD analysis is shown in Figure 6. The figure shows that the Karangnunggal bentonite consists of montmorillonite, halloysite, and few amounts of magnetite. The calculation to the peaks that corresponds to each of those minerals shows that the sample is composed of 45 % montmorillonite, 39.30 % quartz, 14.60 % halloysite, and 0.70 % magnetite. The mineral composition of this sample is shown in Table 2.

Chemical Analysis

The chemical analysis (Table 3) shows that the oxides within the bentonite from Karangnunggal are SiO_2 (66.70 %), Al_2O_3 (19.12 %), Fe_2O_3 (0.84 %) and other minor oxide substances. SiO_2 and Al_2O_3 are the main minerals needed as raw materials for ceramics production. On the other hand, Fe_2O_3 has a possible effect that can reduce the brightness of the ceramic (Celik, 2010).

The hardened grayish-white feldspar has been mined in the dispersion area 14.60 ha and fired at 1,400 °C by Jasmas Company, which results in the formation of homogenous bright grey glass liquid.

The greyish and brownish white kaolin consist of iron oxide, which is the result of tuff weathering of Genteng rock member of Jampang formation (Figure 2). The rock was split and fill a certain part of the valley. At 1,400 °C, it shows that the glass has not yet been formed. The colors of the sample at 1,400 °C is red and brown with yellow spots. The samples (BC-1 and BC-2) that were fired at 1,200 °C can be seen in Figure 7.
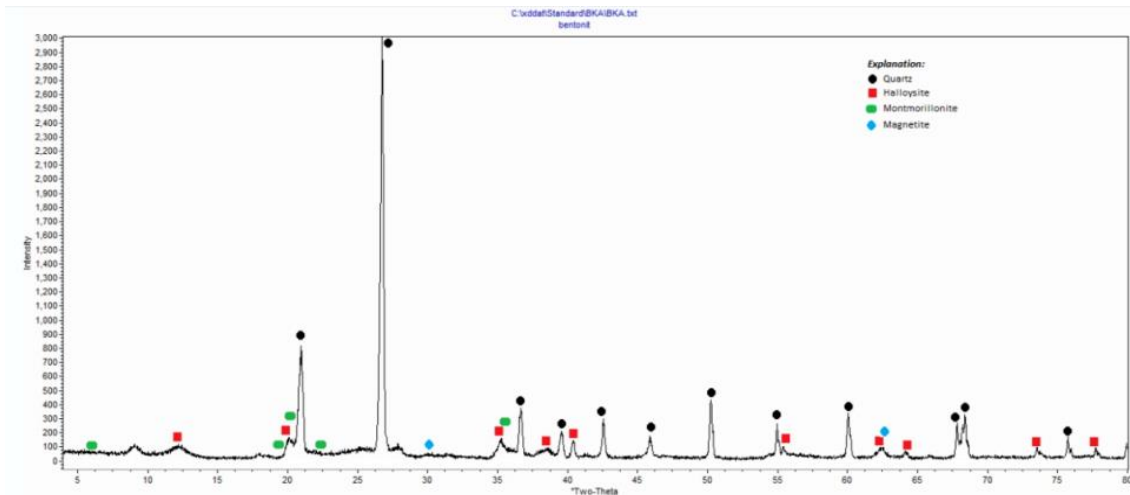
Figure 6. XRD diffractogram of Karangnunggal bentonite

Table 2.   Mineral composition of Karangnunggal bentonite

No	Mineral	Formula	Content (%)
1	Quartz	SiO_2	39.30
2	Montmorillonite	Al_2O_3 4 SiO_2 n H_2O	45.40
3	Halloysite	$Al_2Si_2O_5(OH)_4$	14.60
4	Magnetite	Fe_3O_4	0.70

Table 3.   Chemical composition of raw material to make ceramics

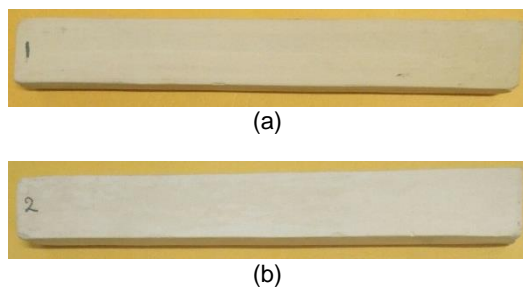| Oxide	Oxide content in the material (%)			
	Bentonite	Kaolin	Feldspar	Silica Sand
SiO_2	71.22	71.82	75.05	88.85
Al_2O_3	14.45	17.20	13.48	3.08
Fe_2O_3	0.84	1.45	0.75	0.46
K_2O	1.02	0.75	2.88	0.80
Na_2O	0.68	1.18	4.06	0.75
CaO	2.40	0.25	0.68	1.15
MgO	1.15	0.30	0.18	0.80
TiO_2	0.25	0.04	0.10	-
MnO	0.03	0.06	0.02	0.02
P_2O_5	0.14	0.62	0.08	0.04
SO_3	0.22	0.45	0.20	0.24
LOI	7.60	5.88	2.52	3.81

(a)

(b)

Figure 7. The samples (a) BC-1 and (b) BC-2, that were fired at 1,200 °C

Result of XRD analysis for samples with the code BC-1 and BC-2 is shown in Figure 8 and Figure 9. The figures show clearly that after being heated at 1200 °C, the mineral within the samples are dominated by quartz and mullite. Quartz possibly was resulted from two sources, silica sand and some parts of bentonite. Since the quartz is thermodynamically very stable, it did not undergo the reaction. The peak profiles of quartz in both samples are quite the same.
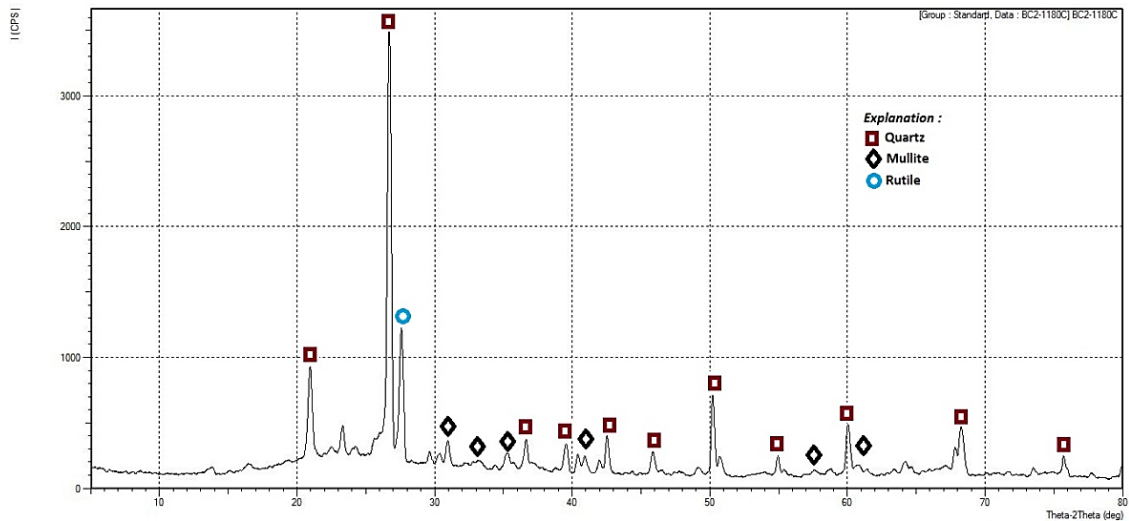
Figure 8. The XRD diffractogram of BC-1 sample that was fired at 1,200 °C
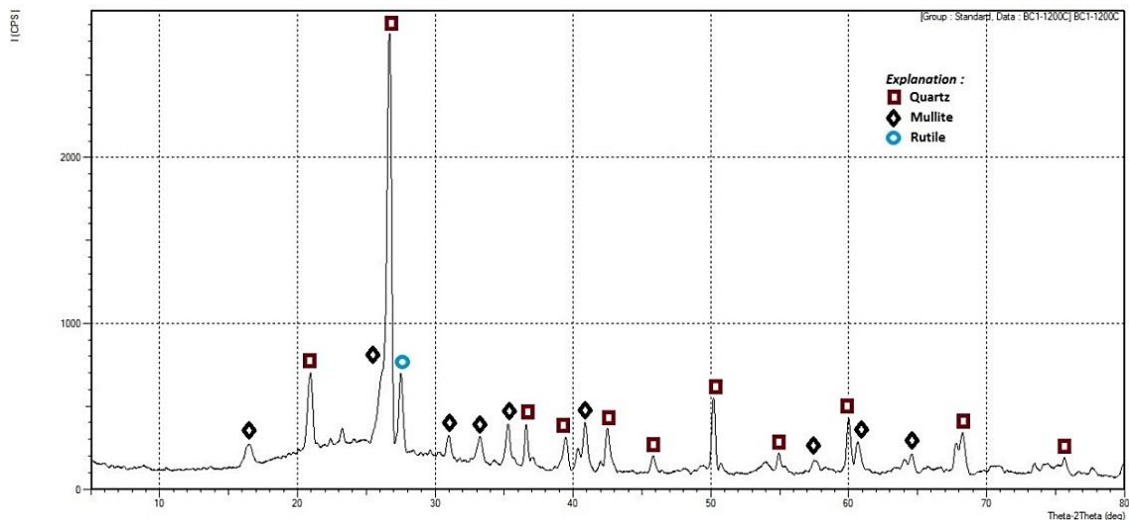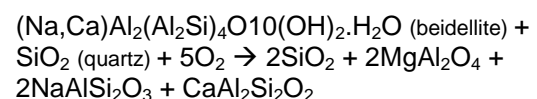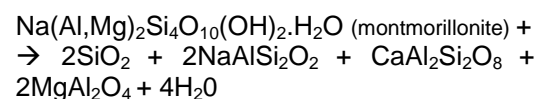

Figure 9. The XRD diffractogram of BC-2 sample that was fired at 1,200 °C

A brief study of the thermally treated bentonite (Zivica and Palou, 2015) has reported that bentonite converted to a microcrystalline variety of hydrous silica, with a general formula $SiOx.H_2O$ after being heated at 650 °C. The continuation of heating until 1200 °C removes H_2O and leaving SiO_2. Thus, the peaks correspond to SiO_2 from samples BC-1 and BC-2 are possibly contributed by both silica sand and silica from the reacted bentonite.

Meanwhile, mullite ($3Al_2O_3.2SiO_2$) can be formed by the reaction of reactive alumina and reactive silica or the reaction of the minerals that contains Al-Si-O, such as montmorillonite, kaolin or bentonite. The study on the thermochemical reaction of montmorillonite with other components has been reported in certain published papers. One of them are Ekosse and Mulaba-Bafibiandi (2008) that has been suggested the reactions at high temperature that involved montmorillonite. The reaction can be written as follows.

$Na(Al,Mg)_2Si_4O_{10}(OH)_2.H_2O$ (montmorillonite) + $\rightarrow$ $2SiO_2$ + $2NaAlSi_2O_2$ + $CaAl_2Si_2O_8$ + $2MgAl_2O_4$ + $4H_2O$

$(Na,Ca)Al_2(Al_2Si)_4O10(OH)_2.H_2O$ (beidellite) + SiO_2 (quartz) + $5O_2$ $\rightarrow$ $2SiO_2$ + $2MgAl_2O_4$ + $2NaAlSi_2O_3$ + $CaAl_2Si_2O_2$

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It can be seen that montmorillonite can actually decompose to more simple compounds such as $MAlSi_2O_3$ or YAl_2O_4 (where M=Na or Ca, Y=Mg). XRD analysis of the sample that was heated at 1200 °C (shown in Figure 8 and Figure 9) shows that such components did not exist. The result of decomposition reaction of montmorillonite is a non-crystalline substance.

On the other hand, halloysite can also decompose to more simple components such as $xAl_2O_3.ySiO_2$. It is highly possible that mullite is the result of halloysite decomposition. The XRD patterns of heated samples (BC-1 and BC-2), that contain halloysite, supported this possibility. The reaction of halloysite decomposition can be written as follows (Zivica and Palou, 2015):

$3Al_2Si_2O_5(OH)_4$ (halloysite) + $4O_2$ → $3Al_2O_3.2SiO_2$ (mullite) + $4SiO_2$ + $6H_2O$
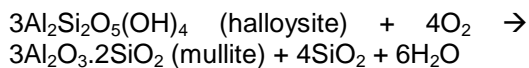
The mineral composition of samples (BC-1 and BC-2) is presented in Table 4 and Table 5. Table 4 show that at the addition of 10 % bentonite, the mullite content increases whereas quartz content decreases. The chemical composition (Table 3) of bentonite is $Al_2O_{34}SiO_2H_2O$, which is built by Al_2O_3 and SiO_2 minerals. Meanwhile, kaolin also has 17.20 % Al_2O_3 and 71.82 % SiO_2. The quartz and feldspar that were used in the experiment also have 88.85 % and 75.05 % SiO_2, respectively. The high content of Al_2O_3 and SiO_2 in each raw material leads to the formation of newly minerals, mullite, and quartz, at 1,180 °C. The formation of these newly materials has also reported in a research work reported by Zivica and Palou (2015) during firing.

The increase of firing temperature until 1,200 °C increases mullite content (to become 52.90%) and decreases the quartz content (down to 34.71 %).

Result of ceramics test after being fired at 1,200 °C is shown in Table 6. The table shows that the absorption of water and the porosity decrease with the increase in firing temperature. It is caused by the increase of glass phase formation. The liquid phase contributes to the sintering process to increase the consolidation ability of the particles at high temperature. The optimum temperature that results in the maximum strength is at the level in which absorption of water is the lowest one. It is important to be noticed that the maximum strength can be obtained from the firing at the same temperature. The highest flexural strength (that is agree with the highest optimum density) is 254.70 kg/cm^2 at 10% bentonite and firing temperature 1,200 °C.

According to Rasin and Hamad (2012), the heating of bentonite at 1,200-1,250 °C result in the increase of porosity. But, further heating at 1,300 °C decreases the porosity. The porosity decrease is caused by the lack of fluid phase that fills the void. The porosity decrease makes the fusion of the ceramic body and the formation of a glass phase take place. The formation of the glass phase contributes to the decrease of open pores in the ceramic. This phase aids sintering takes place. Fast sintering causes an increase in thermal flexure up to 254.70 kg/cm^2 and a decrease in water absorption to 3.98 %.

Table 4.   Mineral composition of BC-1 sample that was fired at 1,200 °C

No	Mineral	Formula	Content (%)
1	Quartz	SiO_2	43.60
2	Mullite	$Al_2O_3SiO_2$	38.30
3	Rutile	TiO_2	18.10

Table 5.   Mineral composition of BC-2 sample that was fired at 1,200 °C

No	Mineral	Formula	Content (%)
1	Quartz	SiO_2	34.70
2	Mullite	$Al_2O_3SiO_2$	52.90
3	Rutile	TiO_2	12.50

Table 6.   Result of ceramics test after being fired at 1,200 °C

Sample Code	Dry Shrinkage (%)	Firing Shrinkage (%)	Dry Flexural Strength (kg/cm^2)	Thermal Flexural Strength (kg/cm^2)	Water Absorption (%)
BC-0	5.29	3.84	36.85	218.85	4.72
BC-1	5.81	4.15	39.70	237.49	4.43
BC-2	6.17	4.47	42.16	254.70	3.98
BC-3	6.24	5.06	43.58	251.96	3.87

CONCLUSIONS

- Based on the chemical and physical characterization, the property of Karangnunggal bentonite, bentonite can be used as an additive material to produce high strength ceramics.
- The maximum flexural strength that can be achieved is 254.70 kg/cm^2 at 10% bentonite and 1,200 °C combustion temperature.
- The experimental result showed that the formulation 55 % kaolin, 20 % quartz, 15 % feldspar, and 10 % bentonite had the highest flexure and the lowest moisture absorption of both were 254.70 kg/cm^2 and 3.98%, respectively.

ACKNOWLEDGEMENTS

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