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PREPARATION AND CHARACTERIZATION OF PHOSPHATE-SLUDGE KAOLIN MIXTURE FOR CERAMICS BRICKS

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ABSTRACT

Phosphate Sludge (PS) waste has been a problem in metal surface finishing industry. The waste cannot be dumped in landfill due to the metal content. Valorisation of the waste will be beneficial in a way that it conserves natural reserves and reduces energy consumption. This paper describes the attempt of utilization of PS by mixing it in kaolin in preparation of ceramic bricks. A series of experiments showed that mixtures containing between 25–50 mass % PS sintered at 1200°C attained the highest compressive strength of >25 MPa. X-ray diffractions (XRD) showed that the presence of PS hindered the formation of mullite, the phase that contribute to strength in Al_2O_3–SiO_2 kaolin system. In the mixture of 1:1 kaolin: PS fired at 1200°C, cristobalite was formed, instead of mullite, as observed in the XRD patterns.

Keywords: Ceramics; Firing; Kaolin; Phosphate-sludge

1. INTRODUCTION

Zinc phosphate is widely used in the finishing process of metal industries such as automotive, steel furniture, houseware, electrical equipment, construction, etc., due to its capability to protect the base metal from corrosion and to enhance paint adhesion. However, the use of zinc phosphate produces waste in the form of liquid, which can be treated and disposed to the environment, and solid sediment known as phosphate sludge (PS) which is harmful if not properly treated. PS is a mixture of iron and zinc salt of phosphoric acid with the general formula $ZnFe_{7/3}(PO_4)_3$, also called as phosphophylite. PS mass range consists mainly of, in weight percentage, ~20 iron, 50-55 phosphorus, and ~10 zinc (Narayanan, 2005). According to the US Environmental Agency (USEPA) PS is considered hazardous and therefore must be encapsulated before disposing in landfills. The high cost of PS handling that cannot be disposed into drains and the environment directly, has been a problem that demands an urgent solution.

Effort to recover PS involved leaching and extraction processes in physics and chemistry or solidification (Kuo, 2012; Navarro-Blasco et al., 2015). Reuse and recycling of the materials was focused on the recovery of zinc, iron and phosphate. Several methods for reclaiming phosphate has been patented (Narayanan, 2005), however none can be claimed to be the most effective method in terms of benefits versus energy consumption or cost. Utilization of this solid waste into building materials becomes an alternative to recovery. Unlike the ordinary building materials, the capability of, especially hazardous, metals containment within the method used is of prime important. Some of use of PS reported were as an aggregate for

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concrete (Doğan & Karpuzcu, 2010; Loutou et al., 2013); as an ingredient in the manufacture of clinker in cement industry (Caponero &Tenório, 2000; Lin et al., 2009); and in clay bricks manufacture (Bersch et al., 2012).

The presence of phosphate and iron oxides affects sintering temperature hence phase(s) formation, mechanical and physical properties of the products. A study found that the addition of phosphate compounds into kaolin decreased sintering temperature of up to 200ºC without decreasing rupture strength (Little et al., 2008). Little and colleagues reported an experiment by adding 10 weight % of dried PS of tri-cationic phosphate solution into fly ash ceramic, resulted in significantly lower sintering temperature of up to 75ºC (Little et al., 2008). Besides lowering the sintering temperature, the addition of PS also reduced the level of arsenic leaching (Little et al., 2008). In addition, the presence of a metal with a low melting point such as zinc, contributed to the increase of liquid phase at lower temperatures (Little et al., 2008). PS could also be added by 10−20 weight % in concrete for applications that do not requires high strength (Ucaroglu & Talinli, 2012). The presence of iron oxides in kaolin lowers the sintering temperature of up to 50°C (Nana et al., 2013) and resulted in solidified phase of mullite and cristobalite (Little et al., 2008). It was also found that mullite crystal in lath-like and needle-like shape occurred in samples containing iron oxide (Guo, 2010). Flexural strength of samples with a high content of iron oxide found to be higher than the samples with a low content of iron oxide (Michot et al., 2008).

In this work, kaolin- based ceramic brick with the addition of PS has been prepared and characterized. The mass optimization of PS utilization is the main focus in this study. Sintering temperature related to optimum mixture composition of PS-kaolin was varied to obtain the best compressive strength at the lowest sintering temperatures, hence the minimum energy consumption.

2. METHODOLOGY

2.1. Raw Materials

PS used in these experiments were supplied from a metal surface treatment company in Banten Province, Indonesia, while kaolin was purchased from PT RAK Minerals Indonesia under the trademark of Cerafill. The kaolin, with a size of 325 mesh, was originated from Bangka island, Indonesia. Chemical compositions, analysed using X ray fluorescence spectroscopy, of both raw materials are presented in Table 1 and 2.

2.2. Specimens Preparation

PS was cloth-filtered to reduce excessive water, washed and then dried at 110ºC until sufficiently dried to be milled. The milled PS was mashed by hand mortar and sieved to 100 mesh. PS and kaolin at specified mixing ratios were mixed using hand rotating drum and casted in molds with dimensions according to the tests. After casting, the specimens were dried in an oven at 110ºC for at least 24 hours. Cubes of 50×50×50 mm^3 were prepared for compression test. Compressive strength values presented were from three best specimens. For each composition and sintering condition, materials from broken compression test samples were taken for x-ray diffraction and scanning electron microscopy (SEM). Variations of composition, sintering temperature and sintering time were performed to obtain optimum compressive strength with minimum of energy consumption, i.e. the lowest sintering temperature and time. Sintering was conducted in an electric furnace with a heating rate of 5ºC/min to 500ºC, at 10ºC/min from 500 to 925ºC and at 15ºC/min from 925ºC to the specified sintering temperature.

Table 1 Chemical composition of phosphate sludge

Compound	Mass (%)	Element	Mass (%)
Al_2O_3	0.11	Al	0.06
Fe_2O_3	29.39	Fe	20.56
Na_2O	1.82	Na	1.35
P_2O_5	38.83	P	16.94
LOI	23.70	-	-
ZnO	5.64	Zn	4.53

Table 2 Chemical composition of kaolin

Compound/element	Mass (%)
Al_2O_3	42.3029
SiO_2	55.1546
S	-
K_2O	1.2419
CaO	-
TiO_2	0.2068
MnO	-
Fe_2O_3	1.0902
ZrO_2	-
V_2O_3	0.0037

2.3. Characterization Techniques

Phase analysis using XRD and SEM observation were carried out to understand the phase(s) formation during sintering. Density, water absorption and initial rate of suction (IRS) of the products with the optimum strength were then measured.

XRD was performed using XRD-7000 X Shimadzu Maxima, equipped with a graphite monochromator and using Cu radiation Kα, wavelength (λ) of 1.54 Å. JEOL JSM-6390A SEM equipped with Energy-Dispersive X-ray Spectroscopy (EDS) was utilized for microstructure observation. Density of the specimen was calculated by dividing the mass measured with volume calculated from the specimen dimension. Dimensional measurements were carried out using a calliper while mass of the specimens were weighed using an analytical balance with an accuracy of ± 0.01 gram. Water absorption was calculated using Equation 1 as follows,

$$\%\ absorption = \{100(w_s - w_d)\}/w \tag{1}$$

where w_s counts for saturated mass after soaked in cold water for 24 hours, and w_d is dry mass of specimen before soaking.

Initial Rate of Suction (IRS) was calculated using Equation 2 as follows,

$$IRS = (m_1 - m_2)K \tag{2}$$

where IRS is for initial rate of suction in gr/minute/30in^2 or in gr/minute/193.55 cm^2, in which K=30/Area or K=193.55/Area, respectively.

3. RESULTS AND DISCUSSION

3.1. Compressive Strength

Figure 1 shows the compressive strength of kaolin – PS at various compositions after firing at different temperature and time. Compressive strength values presented were from the best three specimens made at the specified firing condition. Many specimens cracked during firing very probably due to thermal shrinkage. At all compositions, strength increased with increasing firing temperature, however the increase in strength up to 1000^{o}C was not significant. Significant increase occurrred at firing above 1150°C. Accordingly, 1200°C can be considered as a minimum sintering temperature to produce ceramic bricks complying with the required compressive strength of more than 10 MPa.

Figure 2 shows the compressive strength of 2 hours - 1200^{o}C sintered kaolin with 0, 10, 20, 25 and 50 mass % substitution of PS. As shown by the figure, there was a tendency that strength increased with the addition of PS up to 25% after which the strength decreased. However the strength of kaolin without PS was inconsistently lower compared to the same treatment at 1 hour firing as shown in Figure 1. Highest compressive strength of >25 MPa was achieved by specimens prepared with the addition of 25 to 50% of PS fired at 1200^{o}C.

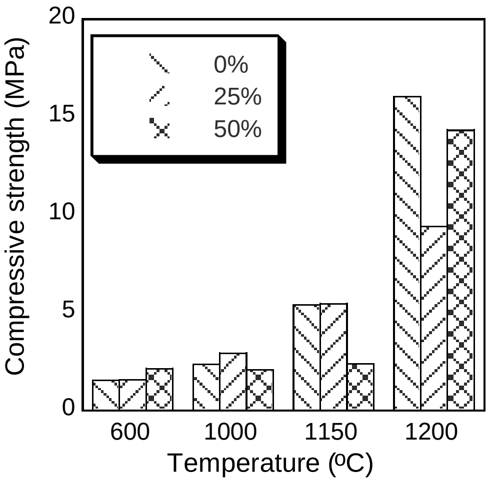


Figure 1 Compressive strength of 0, 25 and 50 mass % PS – kaolin specimens fired at different temperatures for 1 hour sintering

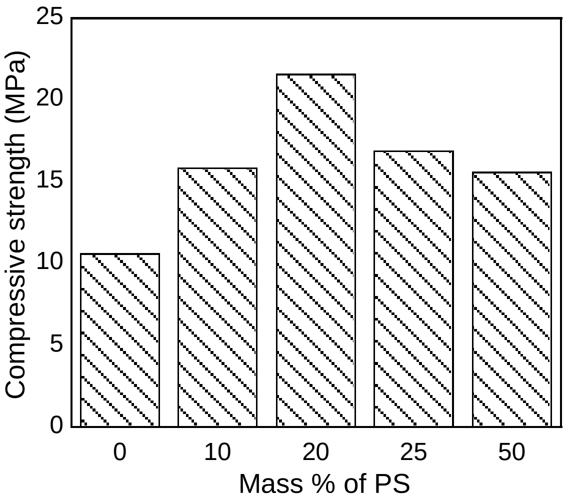
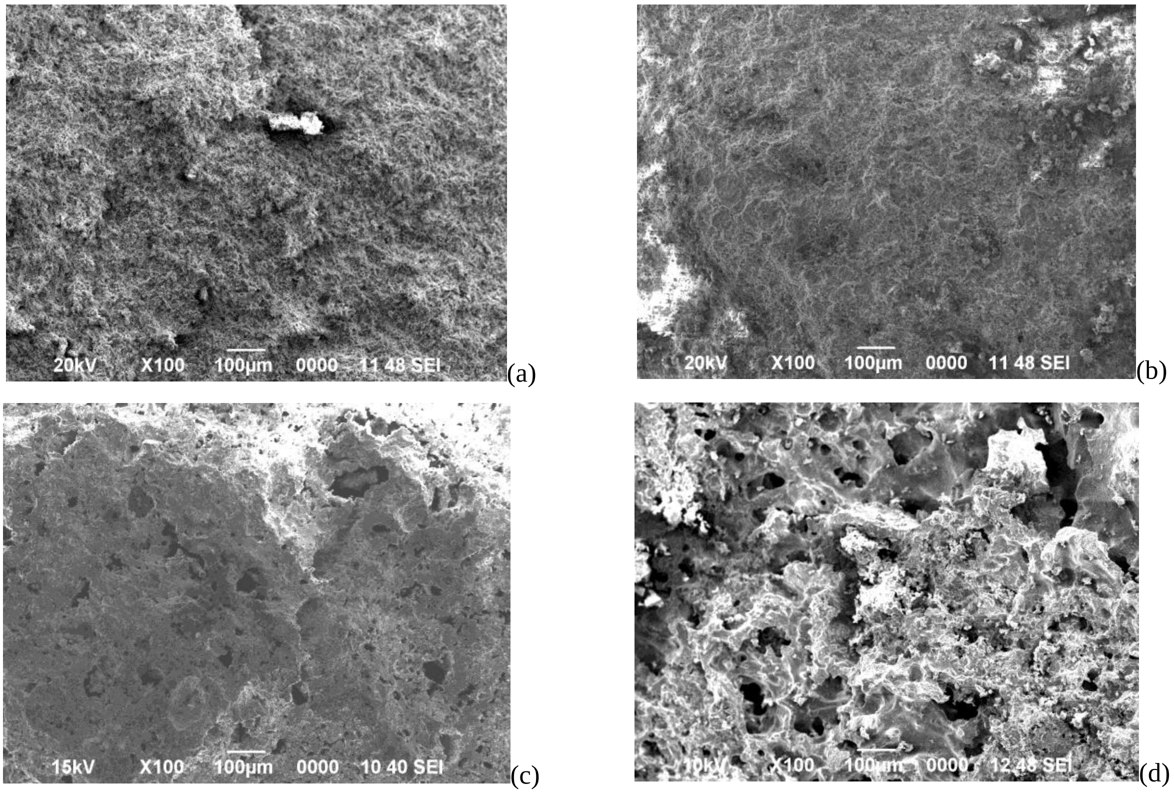


Figure 2 Compressive strength of kaolin - PS specimens fired at 1200^{o}C for 2 hours with different content of PS in mass percent

3.2. Microstructures

Figure 3 shows the fractured surface of 1200^{o}C- fired specimens of PS-kaolin containing 0, 10, 20 and 50% PS. These SEM images were at the same magnification and it shows that specimens with higher content of PS contains more pores. Specimens' surface topography at 0 mass% PS, as shown in Figure 3a appeared denser and did not show any pores. Specimen with 10% PS already showed a few pores, in the image in Figure 3b there were approximately 4 small pores sizing less than 10 µm. Increased addition of PS to 20% in which the specimen's surface image shown in Figure 3c showed much more pores with diameter ranging from 10 to 100 µm. In the clay-PS mixture of 50% as presented in Figure 3d, the specimen was full of large cavities and started to disintegrate. Previous study on PS-fly ash mixture found that PS addition into fly ash specimens resulted in larger cavities than without PS addition, moreover, specimens containing PS experienced bloating (Little et al., 2008). Increased voids size of the specimen can be caused by lower melting point compounds like $Zn(PO_3)_2$, $Zn_3(PO_4)_2$, ZnP_4 and the reduction of Fe_2O_3 into Fe_3O_4 at temperatures >1000°C producing O_2 gas which was then trapped in the specimens. Porosity in the specimens can lead to higher water absorption. On the other hand, another study found that the addition of 10% H_3PO_4 into kaolin significantly lowered porosity (Charfi et al., 2013).



(a) (b) (c) (d)

Figure 3 SEM micrographs of PS-kaolin specimens fired at 1200°C for 2 hours: (a) 0%PS; (b) 10% PS; (c) 20% PS; (d) 50% PS

3.3. X-ray Diffraction

Heating the mixture of 1:1 PS-kaolin, or 50% PS, by weight at elevated temperature of 1150 and 1200^{o}C induced the formation of β cristobalite, a metastable phase formed during cooling of silica, shown on the XRD pattern in Figure 4. Previous study on kaolinite showed that cristobalite was formed at 1050°C following the formation of mullite starting at 950^{o}C (Michot et al., 2008). The expected formation of mullite in the 1:1 PS-kaolin system could not be fulfilled in these experiments. Mullite, a synthetic phase formed upon firing, is desirable in ceramic system of Al_2O_3-SiO_2 due to its contribution to high mechanical properties. In the kaolin system alone, mullite was formed upon firing at 1200°C as confirmed by the XRD pattern presented in Figure 5. Mullite was however formed together with cristobalite, at the presence of PS up to 20% as shown by the XRD pattern in Figure 5. Phases formation in this system agreed with Little and colleagues (Little et al., 2008). The presence of cristobalite in the system was an indication of melting of silica and hence it can be suggested that the strength developed in the the mixture of high PS content was contributed by the formation of low melting glass, rather than mullite, that bound the particles together. It could also explained that the strength of kaolin with PS addition is lower than pure kaolin system.

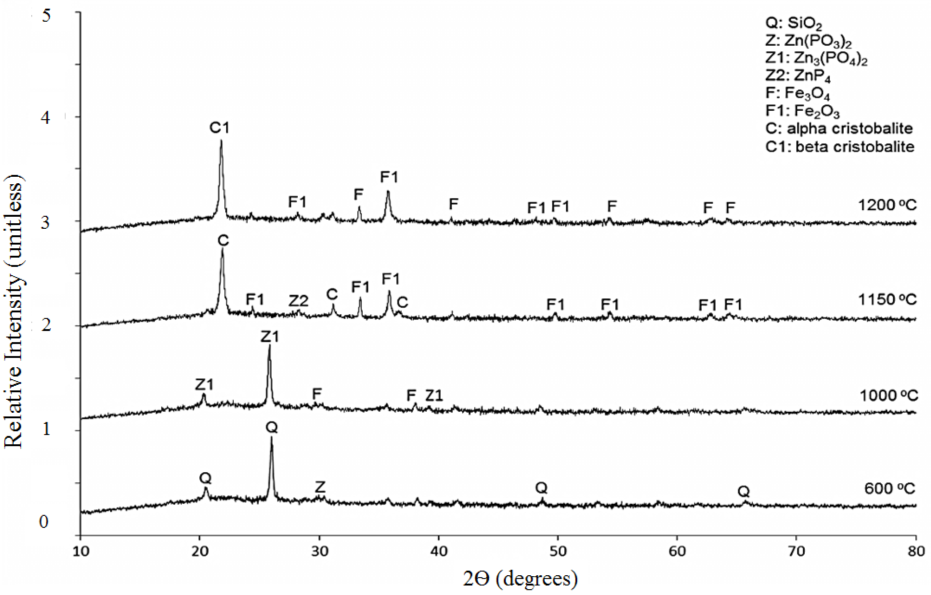


Figure 4 Plot of intensity in counts versus 2θ angle showing The XRD patterns of 1:1 PS – kaolin mixture by mass fired at different temperatures

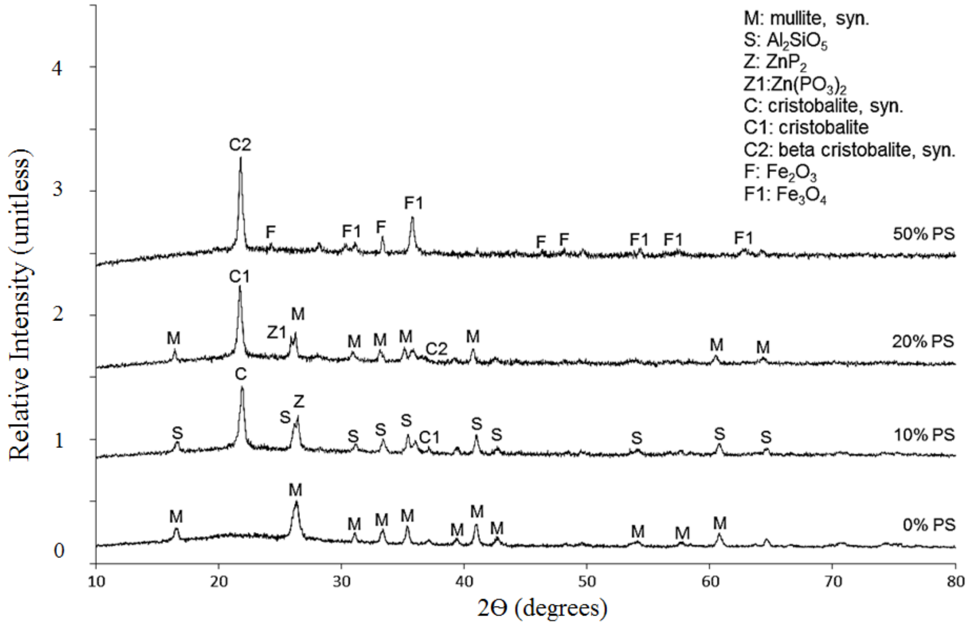


Figure 5 Plot of intensity in counts versus two theta angle XRD patterns of kaolin mixture specimens with various content of PS fired at 1200°C for 2 hours. M=S= mullite or Al_2SiO_5

3.4. Water Absorption and Initial Rate of Suction (IRS)

Mean value of water absorption of specimens containing 10 mass % PS fired at 1200°C was 30.23% which is not in accordance with ASTM C 67-03 “Standard test method for sampling and testing bricks and structural clay tile” which is 13 to 17%. The higher value of water absorption was associated to voids caused by the presence of PS in kaolin mixture as demonstrated by the SEM observation presented in Figure 3. Due to similar reason with water absorption, the IRS of kaolin mixture containing 10 weight% of PS did not meet the required value of <20 g/dm²/min. IRS measurement were performed on 11 samples and gave the mean value of 239 g/dm²/min.

4. CONCLUSION

The fact that many of the specimens cracked and the results of compressive strength suggested that PS – kaolin mixture specimens were sensitive to heating/firing parameters. Before firing at high temperatures, the specimens should be dried, and the firing cycle should be carefully controlled to avoid shrinkage. Based on the experiment results, highest compressive strength of >25 MPa was achieved by specimens prepared with the addition of 25 to 50% of PS fired at 1200^{o}C. The melting of silica was believed to occurred in kaolin – PS mixture and that the melt binding the particles together was the mechanism of strength development. The addition of PS in kaolin induced porosity. SEM observation showed that pore size within the specimens increased with PS. The porosity was believed to be the cause of high values of water absorption and IRS which was below the standard.

5. ACKNOWLEDGEMENT

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