Potassium Silicate Foliar Fertilizer Grade From Geothermal Sludge and Pyrophyllite

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ABSTRACT

Potassium silicate fertilizer grade were successfully produced by direct fusion of silica (SiO₂) and potassium (K₂O) in furnaces at temperatures up to melting point of mixture. The geothermal sludge (98% SiO₂) and the pyrophyllite (95% SiO₂) used as silica sources. For the purposes of the study, potassium silicate fertilizer grade have solids concentrations in the range of 31-37% K₂O, and silica in the range of 48-54% SiO₂. The weight ratio of silicon dioxide/potassium solid being 1:1 to 5:1. Silica from geothermal sludge is amorphous silica whereas from pyrophyllite is crystalline silica. The results showed that the amount of raw materials needed to get the appropriate mol ratio of potassium silicate fertilizer grade are different, as well as the fusion temperature of the furnace. Potassium silicate prepared from potassium hydroxide and amorphous silica from geothermal sludge produced at a low molar ratio (2.5: 1 to 3: 1), potassium required quite small (4:1 in weight ratio), and on a fusion temperature of about 900 °C. Meanwhile, when used crystalline silica from pyrophyllite in addition to the molar ratio high enough (1.4 - 9.4) the temperatures are also high at 1350 °C, so that potassium needed large enough to meet the required molar ratio for the fertilizer grade. The product potassium silicate solid is amorphous with a little trace crystalline.

Keywords: geothermal sludge, pyrophyllite, fusion reaction, potassium silicate solid, fertilizer

INTRODUCTION

Potassium or sodium water glasses are generally produced on an industrial scale by melting together quartz sand and sodium/potassium carbonate in suitable quartz furnaces at temperatures in the range of 1400° to 1500° C with the splitting-off of carbon dioxide. This high-temperature melt process is, however, very costly both in equipment and as regards the amounts of energy required and leads moreover to not inconsiderable emissions, such as dust, nitrogen oxides, and sulfur oxides (US 5238668 A). The alkali extraction and acid precipitation method, low energy method, has also been successfully used to produce silicate solution (Muljani et al, 2014), but this method is less precise when desired solidsilicate product. The hydrothermal reaction of quartz sand with aqueous potassium hydroxide obtained potassium silicate solutions which have SiO₂: K₂O molar ratios of less than 2.75:1. But in this hydrothermal reaction must go through a two-stage process: stage quartz reaction with KOH solution at a temperature of 300 C and quartz reaction stages at a temperature up to melting point (over 1100 °C). SiO₂ structural differences between amorphous and crystalline silica can lead to differences in dissolution behavior. But the physical properties of amorphous silica remains elusive in comparison to crystalline silica based on the more comprehensive quartz dissolution studies. There are also known hydrothermal processes for the production of aqueous potassium silicate solutions that are described in a number of patent applications. Gunnarson at all (2010) reported that the solubility of amorphous silica at 100°C temperature is about 200°C higher than the solubility at higher temperatures. Some mixtures of silica and alkali metal silicates have somewhat lower melting temperatures, than the alkali metal carbonates used (US 282098 A). In this study the use of amorphous silica and alkaline hydroxide for potassium silicate production is expected to reduce heat energy while reducing air pollution, especially carbon dioxide. The mixture of alkaline hydroxide and amorphous silica may lower the melting point of the mixture. It is caused by the solubility of amorphous silica is lower in the crystalline silica. So in the use of alkaline hydroxide the temperature should be maintained below the melt temperature of the product. In a previous study, amorphous silica purification from geothermal sludge in furnace at temperatures up to 1000°C, it is known that the impurities contained in the geothermal sludge much reduced with the increase in temperature of the furnace (Muljani et al, 2011).

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Potassium silicate provides an excellent source of soluble silicon for plants and also provides supplemental potassium, a plant macronutrient (Jayawardana et al, 2014). Potassium silicate is used to strengthen plant resistance to pathogens of fertilizers. The potassium silicate is available both in liquid and in powder form with high solubility to easily produce liquid fertilizers. The powder form can be used to make fertilizers in powder form.

Soluble potassium is completely water soluble and can be used as foliar fertilizers. The foliar fertilizer application of soluble Si has been reported to reduce powdery mildew of cucumber, mask melon, zucchini squash, grapes, and angular leaf spot of beans. The foliar spraying of Si may offer practical and viable mean of reducing plant diseases with low cost (Nolla et al, 2008). It can be synthesized by reacting potassium with silicon dioxide following this reaction:

$$\text{SiO}_2 + 2 \text{KOH} \rightarrow \text{K}_2\text{SiO}_3 + \text{H}_2\text{O}$$

$$\text{SiO}_2 + \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{SiO}_3 + \text{CO}_2$$

The rate of the reaction depends on the ratio of alkali metal carbonate to silicon dioxide and silica structural. Crystalline quartz will dissolve only very slowly in hot water alkaline solutions, while amorphous silicon dioxide, will be readily dissolved at room temperatures (Robert et al, 1977). Although research on the production of potassium silicate much has been done but there is no comprehensive information related to energy efficiency and economy. This study will assess the effect of the raw materials and the need for potash which can reduce the energy and raw materials.

The aim of this study is to provide a process for production of potassium silicate foliar fertilizer that have potassium concentrations in the range of 31-37% K₂O, and silica in the range of 48-54% SiO₂ by the fusion reaction of silicon dioxide with potash. The crystalline silicon dioxide (pyrophyllite) and amorphous silicon dioxide (geothermal sludge) are used in the weight ratio of silicon dioxide/potash. Which molar ratio is used for a specific application depends on the desired properties the silicate has to impart on the products and economic impact.

### METHODOLOGY

**Potassium silicate production**

Silicon dioxide is obtained from geothermal sludge and pyrophyllite. Geothermal sludge is the solid waste from the geothermal plant that is located in Dieng, Central Java, Indonesia. While pyrophyllite is mined from Malang, East Java, Indonesia. X-ray fluorescence analysis showed successive silica content of about 98% SiO₂ in the geothermal sludge and about 85% SiO₂ in the pyrophyllite. To increase levels of silica in pyrophyllite is necessary to use hydrochloric acid leaching.

and to enhance agricultural productivity. Here a potassium silicate is proposed that can be adapted by adjusting physico-chemical properties as requested by the formula, 0.5 N HCl was used to remove impurities in pyrophyllite, that its purity reaches 95% SiO₂.

![Figure 1. X-ray diffraction (XRD) patterns of silica from geothermal sludge](image1.png)

**Figure 1.** X-ray diffraction (XRD) patterns of silica from geothermal sludge.

**X-ray diffraction (XRD) pattern have shown that the silica from geothermal sludge is amorphous (Fig. 1) and silica from pyrophyllite is crystalline (Fig. 2). The silica intensity (7500) is very high at 26° compared to 21° which is 1500 only. However, the graphs obtained in this essay demonstrated that the pyrophyllite had a high reactivity due to the large amount of crystallinity peaks found in the charts.**

![Figure 2. X-ray diffraction (XRD) patterns of silica from pyrophyllite](image2.png)

**Figure 2.** X-ray diffraction (XRD) patterns of silica from pyrophylle.

Pyrophyllite is a silicate that has a high melting point and has high affinity with metal oxide such as potassium oxide and calcium oxide. The high affinity of pyrophyllite with metal oxide may result in the formation of new compound of potassium silicate and calcium silicate which is useful for the fertilizer production.

**Characterization**

**X-ray diffraction**

X-ray diffraction was used to determine the crystallinity of pyrophyllite samples using XPERT PRO diffractometer (Philips, USA). The X-ray diffraction patterns were measured in the 2θ range of 10° to 90° with a step size of 0.02°. The X-ray diffraction pattern was analyzed using the X'Pert HighScore software to determine the crystallinity of pyrophyllite.

**RESULTS**

Fig. 3 shows the X-ray diffraction pattern of the pyrophyllite sample, where the peaks are well-defined, indicating high crystallinity. The peaks correspond to the characteristic diffraction peaks of pyrophyllite, which are located at 2θ values of approximately 9°, 21°, and 38°. These peaks are attributed to the (001), (002), and (003) planes, respectively.
The potassium geothermal sludge and pyrophyllite was crushed and sieved through 100-mesh sieves. KOHandK₂CO₃is a source of potassium for the formation of potassium silicate. Silicon dioxide and potassium mixed by variation of the weight ratio of silica versus potash in the range of 1:1 to 5:1. The potassium silicate obtained in different grades should have a chemical formula of K₂SiO₃. Fusion in the furnace done such that the resulting products only melted but still solid form. Fusion reaction over a range of temperatures below the melting point of the mixture until it reaches the melting point. The powder of silica (geothermal sludge or pyrophyllite) and potassium mixed and then in sprinkling water until the mixture was slightly clump so not much lost powder when hot air that blows touching the mixture. Campuran yang sedikit basah dimasukkan kedalam furnance untuk direaksikan pada suhu 600 °C hingga 1000 °C.

Characterization

X-ray diffraction (XRD) patterns of the potassium silicate were obtained using an X-ray diffractometer (X'pert, Phillips). The composition of silicon dioxide and potassium silicate was analyzed by X-ray fluorescence spectrometry (XRF) and energy dispersive X-ray fluorescence spectrometry (EDXRF, Minipal 4, PANalytical). Scanning electron microscopy (SEM) was used to observe the morphology of the product samples.

RESULTS AND DISCUSSIONS

Fig. 3 showed the correlation of raw material ratio (SiO₂/K₂O) to the concentrations of silica and potassium prepared by K₂CO₃. The concentration of SiO₂ and K₂O on potassium silicate from geothermal sludge and pyrophyllite following the change of raw material ratio SiO₂/K₂O. No difference significantly for SiO₂ concentration in the potassium silicate produced from these two types of raw materials, but there are significant differences in the concentration of potassium in potassium silicate product. This shows that the potassium silicate produced from geothermal sludge and pyrophyllite have different grade ratio in the sameraw material ratio (SiO₂/K₂O).

Figure 2. X-ray diffraction (XRD) patterns of silica from pyrophyllite.

Figure 3. The correlation of raw materials ratio (SiO₂/K₂O) to the concentrations of silica and potassium in potassium silicate product prepared by K₂CO₃.

Fig. 4 showed the effect of raw materials ratio on the concentration of potassium silicate prepared by KOH and K₂CO₃. KOH provides the amount of K₂O in potassium silicate which is slightly larger than K₂CO₃. The concentration of K₂O in potassium silicate produced from pyrophyllite lower than that produced from geothermal sludge. In raw materials ratio 3:1 the concentration of K₂O is 44.7% prepared by geothermal sludge and KOH, and 24.8% prepared by pyrophyllite and KOH. This indicated that the consumption of potassium prepared by pyrophyllite larger than prepared by geothermal sludge for the same expected molar ratio.
Figure 4. The effect of raw materials on the concentrations of potassium silicate solids.

Characteristics of potassussilicate solids is characterized by SiO2: K2O molar ratio. Fig. 5 showed the effect of raw materials on the molar ratio SiO2:K2O.

Figure 5. The effect of raw materials ratio on the molar ratio SiO2:K2O.

Potassium silicate prepared by geothermal sludge and KOH has molar ratio in the range of 0.6-3.1. Less than the molar ratio of potassium silicate from pyrophyllite is in the range of 1.4-9.4. While K2CO3 produces potassium silicate with a molar ratio that is slightly lower than KOH in the range of 0.6-4.1. Amorphous silica from geothermal sludge facilitates the process of mixing and reaction. Potassium silicate solid prepared by geothermal sludge in accordance with the grade of fertilizer produced on the raw material weight ratio of 4:1 with a molar ratio 2.5:1 for the use of KOH, and the raw material weight ratio of 3:1 with a molar ratio 2.33:1 for the use of K2CO3.

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Figure 6. X-ray diffraction (XRD) patterns of potassium silicate solids on the 1:1 weight ratio.

Figure 7. X-ray diffraction patterns of potassium silicate solids prepared by the 4:1 weight ratio.

Diffraction pattern of solid potassium silicate produced from geothermal sludge using OH and K2CO3 in the weight ratio of 1:1 is shown in Figure 5. The both samples showed amorphous nature but the little silica peak at 22° (JCPDS 46-1045). The contrast in thermal reactions increased to 4:1 as diffraction pattern shown in Figure 5. The silica intensity is very high (1300) at 22° prepared by K2CO3 than prepared by KOH is 200 only. The potassium silicate from KOH samples appears largely amorphous with little traces of crystalline phase.

Figure 8. X-ray diffraction patterns of potassium silicate solids prepared by the 4:1 weight ratio.

Diffraction pattern of pyrophyllite 4:1 are shown in Fig. 2 into a reaction between potassium silicate and KOH product can be seen. The yield of geothermal sludge pyrophyllite as the yield prepared by KOH (70-80%). The melting point of geothermal sludge pyrophyllite is at 891°C and the melting point of potassium silicate is at 1100°C using K2CO3 as the melting agent. The melting point of potassium silicate is at 1100°C using pyrophyllite as the melting agent.
Figure 8. X-ray diffraction patterns of potassium silicate solids prepared by pyrophyllite

Diffraction pattern of solid potassium silicate prepared by pyrophyllite using K2CO3 in the weight ratio of 2:1, 3:1, and 4:1 are shown in Fig. 8. Transformation of crystalline structure (Fig. 2) into an amorphous (Fig. 8) occur during the fusion reaction between pyrophyllite (crystalline) with potassium underlay. Amorphous structure on potassium silicate product can increase its solubility.

The yield of potassium silicate solid produced from geothermal sludge (70-80%) is lower than produced from pyrophyllite (91-97%) prepared by KOH. In the other hand the yield of potassium silicate from geothermal sludge prepared by K2CO3 (60-70%) is lower than prepared by KOH (70-80%).

The melting point of potassium carbonate is 891°C and potassium hydroxide is 406°C while the melting point of silica is around 1600 to 1730°C. The difference between the melting point of silica and potassium lead to the melting point of a mixture of both to be different depending on the composition ratio of SiO2/K2O. Figure 8 showed the effect of raw material ratio (SiO2/K2O) on melting temperature. Because potassium hydroxide has the lowest melting point, the melting point of the mixture is in the range of 800°C to 1100°C.

Based on the melting point of a mixture of geothermal silica and potassium in the molar ratio 3:1 to 4:1 the melting temperature up to 900°C using KOH and up to 1100°C using K2CO3. As for the mixture of pyrophyllite and potassium, the molar ratio 2:1 reaches the melting temperature 1200°C using KOH and 1350°C using K2CO3.

Figure 8. Effect of raw materials ratio SiO2/K2O on melting temperature

The SEM images shown in Fig. 9 confirm that the particles of potassium silicate prepared by KOH were smaller and more uniform than those prepared by K2CO3. The size distribution of the particles, as deduced from the SEM images, show that particle size prepared by KOH in the range of 62-145 nm and that prepared by K2CO3 in the range of 40-220 nm.

Fig. 9. SEM images of potassium silicates solid from geothermal sludge prepared by (a) KOH and (b) K2CO3

CONCLUSIONS

Characteristics of potassium silicate which is characterized by molarratio influenced by the type of raw material and potassium salts used. The amount of raw materials needed to get the appropriate molarratio of potassium silicate fertilizer grade are different, as well as the temperature of the furnace. Potassium silicate prepared by potassium hydroxide and amorphous silica from geothermal sludge showed in...
accordance with fertilizer ratio (2.5:1), potassium requirements is quite small and a temperature of about 900°C. Meanwhile, when used crystalline silica from pyrophyllite in addition to the molar ratio high enough (3.5:1) the temperatures are also high at 1350 °C, so that potassium needed large enough to meet the required molar ratio for the fertilizer.

The product potassium silicate solid is amorphous with a little trace crystalline.

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