Potential Application of Silica Mineral from Dieng Mountain in Agriculture Sector to Control the Release Rate of Fertilizer Elements

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Abstract. Silica mineral, which comes along with geothermal fluid in Dieng, is a product of erosion, decomposition and dissolution of silicon oxide based mineral, which is followed by precipitation to form silica mineral. This silica cell structure is non crystalline, and it contains 85.60% silicon oxide, 6.49 volatile elements, and also other oxide elements. Among the direct potential application of this silica is as raw material in slow release fertilizer. Silica in compacted slow release fertilizer is able control the release rate of fertilizer elements. Two type of slow release fertilizer has been made by using silica as the matrix in these slow release fertilizer. The first type is the mixing of ordinary solid fertilizer with Dieng silica, whereas the second one is the mixing of disposal leach water with Dieng silica. The release test shows that both of these modified fertilizers have slow release fertilizer characteristic. The release rate of fertilizer elements (magnesium, potassium, ammonium, and phosphate) can be significantly reduced. The addition of kaolin in the first type of slow release fertilizer makes the release rate of fertilizer elements can be more slowed down. Meanwhile in the second type of slow release fertilizer, the release rate is determined by ratio of silica/hydrogel. The lowest release rate is achieved by sample that has highest ratio of silica/hydrogel.

1. Introduction
Silicon oxide is among the abundant compound in world in the form of silica or silicate mineral [1]. Silicate or silica usually can be found in nature as gangue mineral in some ores such as iron, nickel, gold and bauxite ore [2]. Silica also can be found as disposal mineral in hydrothermal power plant [3]. Silica cell structure is various, but the most reactive silica is the amorphous one [4]. One of the places where non crystalline silica can be found is Dieng Mountain. This non crystalline silica is actually a solid part of geothermal suspension fluid that has been sucked toward the surface of the earth during geothermal power plant activity. Non crystalline silica is formed through erosion and decomposition of crystalline silica along with other mineral, which is followed by dissolution and precipitation of SiO₄²⁻ ion to form non crystalline silica [5]. Up to now, in geothermal power plant, this silica is labeled as by product mineral and it is still treated as disposal.

Silica or silicate can be directly used in some simple but important application after being treated through certain simple physical treatment [6,7,8]. Silica can be used as raw material in slow release fertilizer synthesis through certain physical method [9]. Slow release fertilizer is a new kind of fertilizer, in which the release rate of the elements in fertilizer can be controlled [6,7]. Silica in slow release fertilizer can be used to control the release rate of fertilizer elements. The application of slow
release fertilizer can increase fertilizer efficiency, while at the same time decrease fertilizer cost. From the environmental point of view, the application of slow release fertilizer can also reduce the ground water contamination that is caused by excessive leaching of fertilizer elements [7,9]. The aim of this research is to characterize silica from Geothermal Power Plant Site in Dieng Mountain and also to characterize the slow release fertilizer made by using this silica mineral.

2. Experimental Procedure
Silica mineral used in this research was obtained from hydrothermal power plant site located at Dieng Mountain, Bondowoso, Central Java, Indonesia. This silica is actually the mineral that comes along with geothermal fluid in Dieng. The silica was washed with water to remove the salt prior to drying for 24 hours. The chemical analysis and XRD evaluation of this disposal was conducted through wet analysis and XRD, respectively.

The fertilizer material used in this experiment was commercial NPK fertilizer that is commonly sold in Bandung area, Indonesia. Another source of fertilizer element was disposal leach water that was collected in the Central Disposal Processing Unit located in West Bandung, Indonesia. The elemental composition of NPK and disposal leach water was identified and measured through Atomic Absorption Spectrometry (AAS) and gravimetry analysis.

There are two type of slow release fertilizer we have made. The first type of fertilizer was made by using ordinary solid fertilizer and silica from Dieng. We prepared two formulas by using these raw materials. The first sample (namely A1) consists of silica and ordinary commercial fertilizer. The second sample (namely A2) consists of silica, ordinary commercial fertilizer, and kaolin. The detail composition of both formulas is shown in Table 1. The mixed raw material is pressed and heated at 10 kg/cm² and 80 oC, respectively, for 24 hours.

**Table 1.** Composition of slow release fertilizer synthesized by using commercial fertilizer, silica from Dieng, and kaolin

| Sample Code | Weight of Silica from Dieng (gram) | Weight of Commercial Fertilizer (gram) | Weight of Kaolin (gram) |
|-------------|-----------------------------------|---------------------------------------|------------------------|
| A1          | 130                               | 15                                    | -                      |
| A2          | 90                                | 15                                    | 20                     |

Another type of slow release fertilizer was made by using silica and disposal leach water, as source of fertilizer nutrients. The disposal leach water was obtained from Garbage Disposal Unit in West Bandung District, West Java, Indonesia. The disposal leach water was mixed with hydrogel (commercial hydrogel) and silica from Dieng. The mixing was shaped in the form of tablets and air dried for 24 hours. The total weight of mixed silica-hydrogel and the volume of disposal leach water was fixed at 200 gram and 400 ml, respectively. Table 2 shows 5 (five) sample with different weight ratio of silica and hydrogel.

**Table 2.** The weight variation of silica and hydrogel in the samples

| Sample Code | Weight of Silika (gram) | Weight of Hidrogel (gram) |
|-------------|-------------------------|---------------------------|
| B1          | 190                     | 10                        |
| B2          | 180                     | 20                        |
| B3          | 170                     | 30                        |
| B4          | 160                     | 40                        |
| B5          | 150                     | 50                        |

The release rate of the elements from the fertilizer was determined through the measurement of elements concentration in the beaker glass that was previously filled with sample and de-ionized...
water. For a certain range of time, 2 ml of water was taken, diluted and analyzed through Atomic Absorption Spectrometry (AAS) and Spectrophotometer.

### 3. Result and Discussion

The chemical composition of washed and dried geothermal power plant mineral is shown in Table 3. The table shows that the main compound in the mineral is silicon dioxide (\( \text{SiO}_2 \)). The XRD pattern (Figure 1) shows that the crystal structure of this silica is non-crystalline structure. Non-crystalline silica can be commonly found at geothermal site. The composition of NPK fertilizer used in our experiment is shown in Table 4. The fertilizer elements in this fertilizer are potassium, magnesium, calcium, phosphorous, and volatile compounds (in which ammonium related compounds exist). In our research, the elements that were evaluated are potassium, magnesium, and nitrogen.

#### Table 3. Composition of geothermal power plant mineral

| Components                  | % Weight |
|-----------------------------|----------|
| Silicon dioxide (\( \text{SiO}_2 \)) | 85.60    |
| Alumunium trioxide (\( \text{Al}_2\text{O}_3 \)) | 0.04     |
| Iron trioxide (\( \text{Fe}_2\text{O}_3 \)) | 0.21     |
| Manganese oxide (\( \text{MnO} \)) | 0.05     |
| Magnesium oxide (\( \text{MgO} \)) | 0.03     |
| Calcium oxide (\( \text{CaO} \)) | 0.04     |
| Potassium oxide (\( \text{K}_2\text{O} \)) | 1.86     |
| Sodium oxide (\( \text{Na}_2\text{O} \)) | 0.05     |
| Phosphoric (\( \text{P}_2\text{O}_5 \)) | 0.32     |
| Moisture content (\( \text{H}_2\text{O}^- \)) | 2.25     |
| Volatile content (\( \text{H}_2\text{O}^+ \)) | 6.49     |
| LOI (Ignition Loss) | 11.59    |

#### Table 4. Composition of NPK Fertilizer

| Components                  | % Weight |
|-----------------------------|----------|
| Silicon dioxide (\( \text{SiO}_2 \)) | 0.57     |
| Alumunium trioxide (\( \text{Al}_2\text{O}_3 \)) | 0.64     |
| Iron trioxide (\( \text{Fe}_2\text{O}_3 \)) | 1.02     |
| Manganese oxide (\( \text{MnO} \)) | 0.02     |
| Magnesium oxide (\( \text{MgO} \)) | 0.15     |
| Calcium oxide (\( \text{CaO} \)) | 3.38     |
| Potassium oxide (\( \text{K}_2\text{O} \)) | 18.10    |
| Sodium oxide (\( \text{Na}_2\text{O} \)) | 0.77     |
| Phosphoric (\( \text{P}_2\text{O}_5 \)) | 20.51    |
| Moisture content (\( \text{H}_2\text{O}^- \)) | 0.70     |
| Volatile content (\( \text{H}_2\text{O}^+ \)) | 49.8     |
| LOI (Ignition Loss) | 4.4      |

The XRD analysis to mixed, pressed and heated sample shows that, although it consists of crystalline NPK elements, these samples are amorphous (the figure is not shown). Based on this result, it seems that after being pressed and heated, silica network in the sample was polymerized. The polymerization of silica takes usually takes place when non-crystalline silica is pressed and heated.
[10]. The polymerization of silica traps the fertilizer elements; hence, the release of fertilizer elements is retarded.

The result of the release test of magnesium, potassium, sodium, and ammonium ions from modified fertilizer is shown in Figure 2, Figure 3, Figure 4, and Figure 5, respectively. The release test graph actually represents the release behavior of each element from particular slow release fertilizer.

In the first part of our work, there are two sample of slow release fertilizer we have made, namely A1 and A2. Both of these samples used silica mineral as one of the raw material. The difference is that in Formula A2, some part of silica was replaced by kaolin. Figure 2 shows that magnesium release behavior from both samples seems to follow the behavior of common slow release fertilizer. The release of elements from slow release fertilizer usually follows a polynomial curve. After 2 hours of release test, magnesium concentration is only 80 ppm, but it is eventually increases as test time is increased until it finally reaches a quite stable region after 3 hours. Although both of formulas show similar slow release behavior of magnesium, the quantity of magnesium that is released at each stable region is very different. The stable region of sample A1 is at around 250 ppm, whereas for that of A2 is at around 150 ppm.

Figure 1. XRD pattern of solid part (silica mineral) of hydrothermal suspension.
Figure 2. Release profile of magnesium (Mg) from slow release fertilizer.

Figure 3. Release profile of potassium (K) from slow release fertilizer.

Figure 3 shows the release profile of potassium in water media. The release behavior of potassium is slightly different from that of magnesium. The quantity of potassium being released from slow release fertilizer is larger than that of magnesium. After one hour, the concentration of potassium released from Formula A1 and Formula A2 media reaches 2100 ppm and 8000 ppm, respectively. Both formulas seem to follow the slow release behavior of common slow release fertilizer. The difference in the quantity of magnesium and potassium being released in water media might be caused by difference of the nature of magnesium and potassium containing mineral. Magnesium and potassium containing mineral in ordinary fertilizer is in the form of magnesium and potassium oxide. Magnesium oxide is less soluble in water than potassium [7]. Potassium oxide readily reacts with water to form potassium hydroxide, but in contrast, only small amount of magnesium oxide dissolves in water.
Figure 4. Release profile of Ammonium ($\text{NH}_4^+$) from slow release fertilizer.

Figure 4 shows the release profile of nitrogen, which is represented by ammonium ion. The ammonium ion released from sample A1 and A2 reach stable region in 1 hour at 9000 ppm and 2500 ppm, respectively. It is quite different with those of potassium and magnesium. Unlike ammonium ion, the stable region of magnesium and potassium is reached in longer time, 3 hours for magnesium and 4 hours for potassium. The difference in the time needed to reach stable region might be caused by the difference in solubility value. The time needed to reach stable region for magnesium, potassium, and ammonium is in accordance with the solubility profile of these components. Magnesium oxide is the least soluble component compared to potassium oxide and ammonium hydroxide. Its solubility at 30 °C is only 0.0086 gram/100 ml. Potassium oxide, when it meets with water, decomposes and reacts into potassium hydroxide. This reaction takes time before the product of reaction dissolves in water. On the other hand, ammonium hydroxide dissolves readily in water. Thus, the solubility sequence of these three elements are ammonium hydroxide, potassium oxide, and magnesium oxide.

Another source that contains fertilizer elements is disposal leach water. The composition of disposal leach water is shown in Table 5. The major component in this water are potassium, phosphate, sodium, nitrogen, magnesium, iron and calcium. These component are actually the common components in ordinary fertilizer. In the second part of our work, we have mixed, pressed and dried samples consisting of disposal leach water, silica from Dieng and hydrogel. The mixing, pressing and drying of these samples results in the formation of slow release fertilizer. The result of release test of this fertilizer is presented in Figure 5, and Figure 6.

| Element/Component | Concentration (ppm) |
|-------------------|---------------------|
| Ca                | 3.17                |
| K                 | 2959.55             |
| Mg                | 11.9                |
| Fe                | 9.58                |
| Mn                | 0.45                |
| Na                | 1475.6              |
| N                 | 9440                |
| $\text{PO}_4$     | 765.33              |
| pH                | 8.4                 |
Figure 5. The release profile of ammonium ion from second type fertilizer.

Figure 6. The release profile of phosphate ion from second type fertilizer.

Figure 5 shows the release profile of ammonium from the slow release fertilizer that was synthesized by using disposal leach water and Silica from Dieng. All the samples show similar behavior, in which the ammonium is released at a relatively slow speed. After 100 minutes, all samples show the achievement of a stable region, but the concentration of ammonium at the stable region is quite different. The ascending sequence of ammonium concentration at the stable region in each sample are B3, B2, B1, B4, and B5, with the weight ratio of silica/hydrogel being 6, 9, 19, 4, and 3, respectively. It seems that the highest weight ratio of silica/hydrogel (lowest amount of hydrogel) gives the highest concentration of ammonium. Hydrogel absorbs disposal leach water during slow fertilizer synthesis and releases it during the release test in water. The total mass fraction of liquid/hydrogel determines the amount of disposal leach water in each hydrogel particle. Low fraction of hydrogel leads to a high amount of disposal leach water in each particle. The higher the amount of disposal leach water in each particle, the easier the liquid is released from hydrogel, which leads to the highest ammonium concentration at the lowest ratio of silica/hydrogel. The difference in silica/hydrogel ratio seems to affect...
the concentration of other elements such as phosphate and potassium as shown in Figure 6. The highest amount of phosphate in water is achieved by sample that has lowest ratio of silica/hydrogel.

4. Summary
Silica mineral from geothermal site in Dieng, which is the product of erosion, decomposition, dissolution of silicon oxide based mineral, can be used directly as slow release fertilizer. Two type of fertilizer has been successfully synthesized. The first type of slow release fertilizer consists of silica mineral and ordinary commercial fertilizer; whereas the second type consists of silica mineral and disposal leach water. Both type of synthesized slow release fertilizer shows slow release characteristic. The release rate of magnesium, potassium, ammonium and phosphate can be decreased. The release rate of magnesium, potassium, and ammonium in first type of synthesized slow release fertilizer is determined by the addition of kaolin. The release rate of fertilizer elements in the sample with kaolin is slower than the sample without kaolin. Meanwhile, the release rate of ammonium and phosphate in the second type of synthesized slow release fertilizer is determined by ratio of silica/hydrogel. Sample with highest ratio of silica/hydrogel gives slowest release rate of fertilizer element.

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