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Volcanic Rock of Slamet Volcano as the Potential of Soil Ameliorant

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Abstract – Mount Slamet is an active volcano in Java Island, Indonesia. Slamet volcanic rocks comprise various igneous and pyroclastic rocks, including basaltic lava, andesitic lava, pyroclastic rocks, and intrusions. Geochemical analysis of rocks in the studied area (301300 mE - 303300 mE and 9189400 mN - 9191400 mN) showed the presence of high calcium and iron elements. This geological study aims to determine the potential of material resources contained to be used for agricultural needs. The potential nutrients to be found such as P, K, Mg, Ca, Fe, Ti, Na, Mn, and Si with a DHL conductivity value of 0.0473 - 0.1318 mmhos /cm are classified as non-salinity, which is safe for soil improvement. Then the neutralization value relative to calcite is between 15.45 - 27.27 %, and the abrasion pH value is between 8.05 - 8.91. The agrogeological analysis shows that the Slamet volcanic rock in Baturraden area has good prospects as an ameliorant for highly weathered (acid) soils.

Keywords: Slamet Volcano, agrogeology, nutrients, Baturraden, ameliorant

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Introduction

Background

Nine macronutrients are present in plant tissues with levels of more than 0.1 % dry weight (C, H, O, N, K, Ca, Mg, P, S), and eight micronutrients with levels less than 0.01 % dry weight (Cl, B, Fe, Mn, Zn, Cu, Ni, Mo) (Grusak *et al*., 2016). Besides macro- and micronutrients, some nutrients are categorized as beneficial, such as Co, Na, and Si. The essential nutrients of C, H, and O are obtained from CO_2, H_2O, O_2, and organic matter, respectively. While the other essential nutrients are found in aluminosilicate minerals, ferromagnesian silicates, and other mineral additives in rock (Harley and Gilkes, 2000).

Volcanic products can be found in the form of intrusive rocks, pyroclastics, lava, and lahars which are composed of various igneous rocks that provide minerals (geological materials) (McPhie *et al*., 1993). Rocks are the parent material of soils and are useful in agriculture, which are proven to be nutrient and ameliorant sources. As the source of nutrients, the intrusive, pyroclastic, lava, and lava minerals contain elements of K, P, Ca, S, Na, Cl, Mg (major elements), and Zn, Fe, Zu, Cu, Ni, Mn (minor elements). Ameliorant is defined as a solid material other than the commercial fertilizers that is applied to the soil to improve the physical or chemical properties of the soil to increase soil productivity (FAO, 1984). The solid material in this case is fresh rocks from volcanic material which has the potential to improve the soil with its nutrient content, both major and minor elements (Anda *et al*., 2015).

The ameliorant of material derived from volcanic activities. They have neutralization values, including pH of abrasion and electrical conductivity which can improve the physical and chemical properties of acid soils (Ismangil, 2009).

Slamet Volcano has a long geological history as the mountain that has a short eruption cycle. Rocks which are resulting from volcanic eruptions can explain an overview of the history of eruptions and types of eruptions based on their geochemical composition (Candra *et al.*, 2021). Sutawidjaja and Sukhyar (2009) stated that research on Mount Slamet was limited to volcanological studies, and volcanic geochemistry study (Pasha *et al*., 2015), whilst a research on the potential of Slamet volcanic deposit material resources for agriculture has also been limited. Except for a few nitrogen-specific fertilizers, almost all inorganic fertilizer comes from chemically processed rocks, so-called chemically modified rocks. There are several micronutrients that are often needed by plants, such as copper (Cu), cobalt (Co), and iron (Fe) (Kusdarto, 2008).

Chemical fertilizers make plants grow faster, because they have high levels of substances. However, unused substances react with water and cause an increase in soil acidity. Utilizing rocks as multinutrient fertilizer is a solution to improve the soil acidity and increase soil productivity. The use of natural geological materials, both in the form of soil and in the form of rocks, in crop production systems to increase soil productivity, is often referred to as agrogeology or agrominerals (Straaten, 2002). All materials containing one or more chemical elements that are beneficial to plants can be classified as agrominerals or often also referred to as "Rock Fertilizers" (Benetti, 1983; Appleton, 1990).

Agrogeology aims to utilize the content of minerals and rocks used as fertilizers and ameliorants that are environmentally friendly and sustainable (Straaten, 2007). In agriculture, pyroclastic material is also a growing place for plants, because it contains plant nutrients. Thus, the process of restoring agricultural land can be carried out effectively.

The process of volcanism produces several types of rock that have the potential to act as ameliorants. This research aims to determine the ameliorant potential by means of geochemical analysis of several rocks in the south of Slamet Volcano. The results of geochemical analysis can explain the nutrient content of the volcanic rocks, so that they can be used as ameliorants.

Methods and Materials

Field mapping was used for geological data collection in the field and rock sampling. The geological data obtained was the distribution of rocks, the position of rock layers, morphology, and the level of weathering of rocks (Zaenurrohman and Permanajati, 2019). The laboratory analysis was carried out based on the rock samples that had been collected from the researched area. The laboratory analysis included petrographic analysis, geochemistry, and analysis of agrogeological aspects.

Petrographic analysis was an observation of optical properties using thinly slashed rock samples. This analysis aims to describe the composition and the classification of the rock minerals. Observations of optical properties on parallel nicol (light vibrations parallel to polarizer vibrations) include colour, relief, pleochroism, cleavage, and fractional crystal shapes, twinning, and blackout. This analysis used QAPF diagrams of volcanic rocks (Streckeisen, 1978) and classification of pyroclastic rock types (Pettijohn, 1975).

The geochemical analysis carried out to determine the distribution of chemical elements in rocks is based on the interaction of X-rays with materials using XRF (X-Ray Fluorescence) equipment. The samples used are grinded and mixed, then compressed with a pressing machine using a ring with a diameter of 2.5 cm. The XRF method used to determine the percentage value of the oxide compound by using mass (%) units. The analysis showed the major and minor oxides. The XRF method was widely used in determining the elemental composition of materials (Vicklund, 2008). Determination of mineral composition was based on the composition of the oxide compounds gained from XRF analysis using rock normative analysis, namely CIPW (Cross, Iddings, Pirrson, and Washington) (Warmada *et al*., 2005). The CIPW norm was a sequence of mineral formation and phase relationships of rocks and minerals, using a simplified mineral formula. The results of rock oxide analysis was calculated by applying the CIPW method using the KWare Magma programme.

The analyses of agrogeological potential was conducted by refining rock samples, measuring chemical element content, abrasion pH, electrical conductivity, neutralization value, and rock reserves. The analyzed rock was crushed to a fineness size (particle size), and was used to determine the agrogeological potential. The size of 200 mesh was utilized, because the absorption of rock powder into the soil was faster than the smaller mesh size (less than 200 mesh). The content of chemical elements using a geochemical analysis method was carried out to determine the amount of distribution of chemical elements in rocks based on X-ray interactions with materials using XRF equipment (Rollinson, 1993). The analysis of pH of abrasion used the glass electrode method (Sys *et al*., 1993) with a pH meter to determine the pH of the rock that had been dissolved using distilled water. The electrical conductivity analysis was carried out in the laboratory using a conductivity meter to determine the conductivity value of the rocks, by dissolving them into the distilled water. The value of neutralization or acid-base titration is the reaction between acid and base to reach the equivalence or neutral point. The analysis of neutralization values was carried out to determine the types of rocks that could affect the soil acidity. In this case, mineral calcite becomes the standard, because it has a high neutralization value.

Result and Analysis

Geological mapping showed that the rocks in the researched area were dominated by lava, andesitic intrusion, and lahar deposits. In the studied area, the deposited rock came from the upstream area of Slamet Volcano. The Slamet volcanism produced four volcanic deposits, namely the Slamet lava flow rock, basaltic lava flow, andesitic lava flow, and intrusive lava breccia flow units (Figure 1).

Geochemistry of Rocks

The geochemical study using the X-ray fluorescence (XRF) analysis indicated the major and trace compounds in rocks. The result of analysis, after the normalization is shows in Table 1.

Normative Analysis

The results of normative analysis carried out to know the percentage value of the oxide compound are presented in Table 2.

Magmatic Series of Magma Rock Formation

To determine the magma series of the origin of the rocks in the studied area, the diagram according to Peccerillo and Taylor (1976) were used. Based on the results of plotting the main elements on the SiO_2 vs K_2O diagram, the five rock samples have the range of SiO_2 values of 48.1 - 60.9 wt % and K_2O values of 0.45 - 1.73 wt % (Table 1), which belong to the calc-alkaline magma affinity (Figure 2).

Determination of the Origin of Magma

The characteristics of magma can explain its origin. These properties can be divided into two based on the origin of rocks that interact with magma, namely continents or oceans. Pearce *et al*. (1977) determined the origin of a magma from the content of K_2O, TiO_2, and P_2O_5 depicted in a triangular diagram. Based on the plotting on that diagram (Figure 3), the rocks in the studied area derived from a continental crust.

Based on the tectonic setting by Mullen (1983), the source of magma forming-rocks is

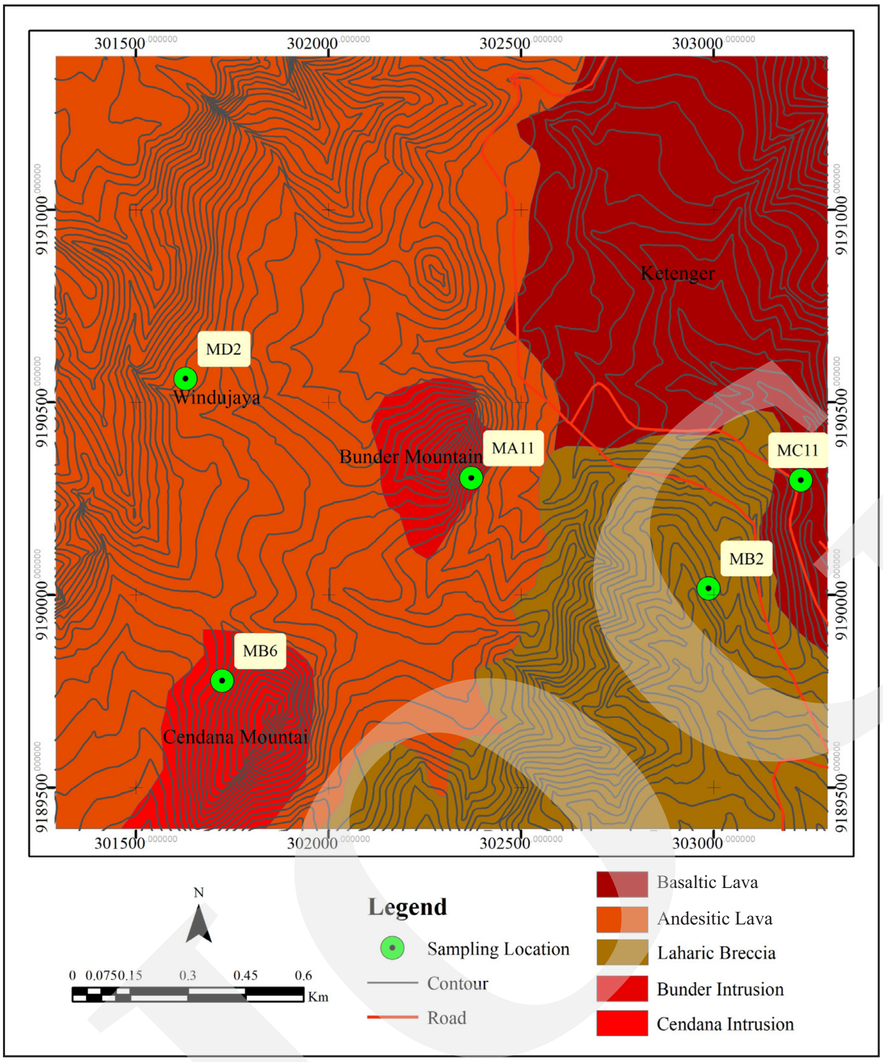


Figure 1 Geological map and sampling locations.

Table 1. Percentage of Oxide Compound from X-ray Fluorescence (XRF) Analysis

Compound	Rocks (%)				
	Basalt lava (MC11)	**Andesite lava (MD2)**	**Laharic breccia (MB2)**	**Bunder intrusion (MA11)**	**Cendana intrusion (MB6)**
SiO_2	48.1	60	51.5	59.6	60.9
Al_2O_3	20.5	21.7	19.7	21.3	23.2
Fe_2O_3	13.7	7.58	12	7.74	7
CaO	11.4	6.75	10	7.61	5.66
MgO	3.17	0.8	4.93	1.37	0.05
TiO_2	1.49	0.81	0.86	0.64	0.51
K_2O	0.82	1.73	0.45	1.11	1.49
P_2O_5	0.2	0.24	0.2	0.21	0.18
Na_2O	-	-	-	-	-
MnO	0.22	0.15	0.15	0.18	0.15
FeO*	12.33	6.82	10.8	7	6.3

Table 2. Mineral Composition of the Rocks

Minerals	Rocks (%)				
	Basaltic lava (MC11)	**Andesitic lava (MD2)**	**Laharic breccia (MB2)**	**Bunder intrusion (MA11)**	**Cendana intrusion (MB6)**
Diopside	1.49	-	-	-	-
Corundum	-	8.14	1.51	6.78	11.83
Orthoclase	4.86	10.22	2.66	6.57	8.87
Anorthite	53.72	31.94	48.41	36.45	27.12
Hyphersthene	26.7	12.7	30.02	14.96	10.65
Ilmenite	2.85	1.54	1.64	1.22	0.98
Quartz	7.95	38.78	13.57	32.47	39.12
Apatite	0.44	0.52	0.44	0.47	0.4
Magnetite	2.00	1.35	1.75	7.81	1.03

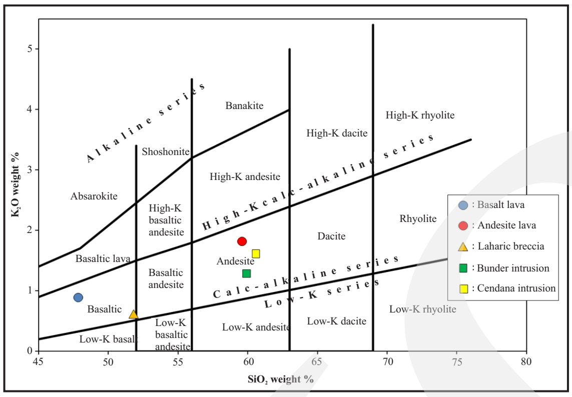


Figure 2. Plotting K_2O vs. SiO_2 of rocks on the diagram after Peccerillo and Taylor (1976).

divided into five types, *i.e.* Mid-Oceanic Ridge Basalt, Island-Arc Tholeiite, Island-Arc Calc-Alkaline Basalt, Oceanic-Island Tholeiite, and Oceanic-Island Alkaline Basalt (Figure 4). Determination of the origin of this magma based on the percentage of TiO_2, 10X MnO, and 10X P_2O_5 plotted in a triangular diagram. Based on the triangle diagram (Mullen, 1983), the origin of the magma in the studied area is the island-arc tholeiite and island-arc calc-alkaline basalt.

Agrogeology Potential

The agrogeological potential in this study aimed at the fineness (particle size) of rock grains as a soil amendment (advanced weathering). The content determination of the chemical elements were beneficial to plants (nutrients), electrical conductivity of rock powder, pH of abrasion, and neutralization value.

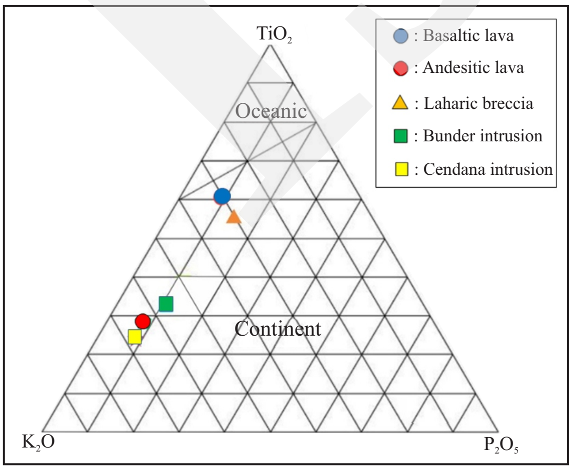


Figure 3 Plotting of rocks origin on the diagram after Pearce *et al*. (1977).

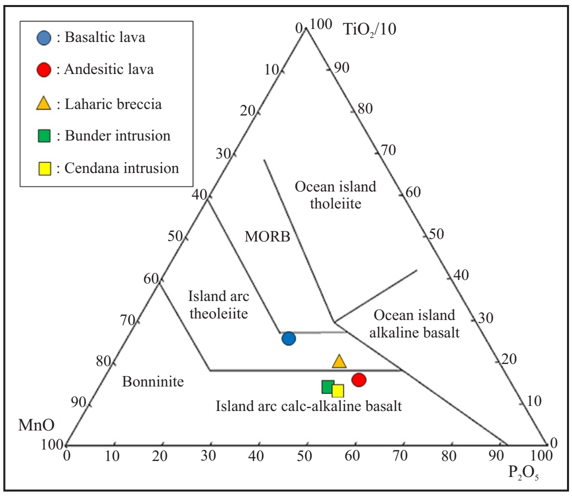


Figure 4. Plotting of rocks on the tectonic setting diagram after Mullen (1983).

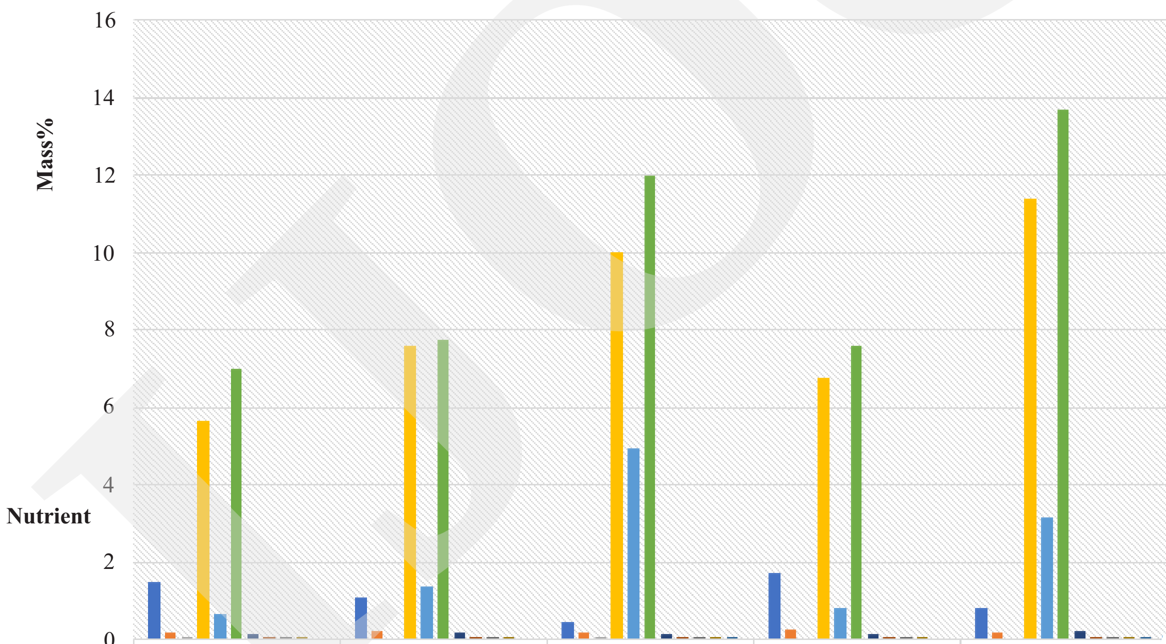
Nutrients for Plants

The analysis results of X-ray fluoresence (XRF) of the five rocks as presented in Table 3 show that the average rocks contain basaltic lava > laharic > intrusion > andesitic lava. The analyzed values of the nutrients contained in the rock are in accordance with the process of rock formation from basalt to andesite. In basaltic lava, the Ca, Mg, Zn, Cl, Fe, Mn, and Cu contents are greater than in laharic breccia, intrusion, and andesitic lava. This is in accordance with the rules of magma crystallization sequence based on the theory of temperature decrease or called the Bowen series (Bowen,1922). In laharic breccia, the nutrient value content tends to be lower than other rocks, because the composition of laharic breccia is the result of mixing andesite and basaltic rocks. Its formation was influenced by the accumulation of materials such as rocks, wood, water, gas, and others.

Electrical Conductivity

The results of research analysis conducted , (Table 4) show that the lowest rock conductivity value is 47.3 S/cm or 0.0473 mmhos/cm with 30.27 dissolved salts, and the highest conductivity value is 131.8 S/cm or 0.1318 mmhos/cm with 84.35 dissolved salt. The conductivity value is influenced by the cation charge contained in geological materials. These cations were lone pairs of electrons that dissolve in water. Dissolved cations are dissolved salts. Thus, the higher the

Table 3. Values and Bar Graphs of Nutrient Content in the Rocks based on Electrical Conductivity Analysis



Nutrient	Cendana intrusion	Bunder intrusion	Laharic breccia	Andesitic lava	Basaltic lava
Potassium	1.49	1.11	0.453	1.73	0.82
Phosphor	0.176	0.214	0.201	0.243	0.2
Sulfur	0.0224	0	0.271	0	0
Calcium	5.66	7.61	10	6.75	11.4
Magnesium	0.652	1.37	4.93	0.801	3.17
Iron	7	7.74	12	7.58	13.7
Manganese	0.151	0.185	0.149	0.155	0.243
Chlorine	0.0136	0.061	0.0135	0.0193	0.0274
Zinc	0.0104	0.012	0.0133	0.0111	0.0157
Copper	0.005	0.005	0.012	0.0066	0.0217
Nickel	0	0	0.0036	0	0.0115

conductivity value, the higher the dissolved salt content, or vice versa. In Table 4, the value of laharic breccia dissolved salt is 84.35 which is the highest compared to the others. This is because laharic breccia is a breakdown and the mixing of previous rocks, namely andesites. Based on the salinity classification according to Taylor (1991), the five rock samples are still classified as non-salinity. Thus, they are safe as soil nutrient improvements (ameliorant) and are not harmful for plants.

Table 4. Electrical Conductivity Value of Rock Samples

Rocks sample	Average (µ S/cm)*	Dissolved salt (mg salt/l)**
Basaltic lava	60,8 ± 2,14	38,91
Andesitic lava	115 ± 3,65	73,60
Laharic breccia	131,8 ± 0,38	84,35
Bunder intrusion	47,3 ± 1,61	30,27
Cendana intrusion	58,2 ± 3,55	37,25
Calcite	73,1 ± 0,35	46,78

Abrasion pH

Abrasion pH analysis was carried out in the laboratory using a pH meter to determine the pH of the rock that has been dissolved using distilled water. The results of analysis presented in Table 5, tend to indicate that the abrasion pH of those five samples has a value above 7, which is influenced by the composition of rock-forming minerals. The results of the normative analysis comprising minerals that have an abrasion pH above 7 such as diopside, quartz, anorthite, orthoclase, hypersthene, magnetite, apatite, ilmenite, and corundum, are included in the pH value of mineral abrasion (Stevens and Carron, 1948, *in* Noble and Lottermoser, 2017).

Table 5. pH Value of Rock Sample Abrasion

Rocks sample	Average
Basalt lava	8,34 ± 0,07
Andesite lava	8,91 ± 0,07
Laharic breccia	8,81 ± 0,02
Bunder intrusion	8,16 ± 0,06
Cendana intrusion	8,05 ± 0,05
Calcite	8,87 ± 0,05

The result of petrographic analysis on abrasion pH values (Stevens and Carron, 1948) of the five rock samples are as follows:

- Basalt lava containing plagioclas mineral type labradorite having an abrasion pH of 8 - 9 with a composition of 60 %, and biotite having an abrasion pH of 8 - 9 with a composition of 10 %.
- Biotite minerals in the laharic breccia fragments having an abrasion pH of 8 - 9 with a composition of 20 % and quartz having an abrasion pH of 6 - 7 with a composition of 5 %. Laharic breccia in the matrix containing hornblende minerals having an abrasion pH of 10 with a composition of 10 %, and pyroxene mineral having an abrasion pH of 10 with a composition of 10 %.
- Cendana intrusion containing biotite mineral having an abrasion pH of 8 - 9 with a composition of 20 %, and quartz having an abrasion pH of 6 - 7 with a composition of 5 %
- Bunder intrusion containing pyroxene minerals having an abrasion pH of 10 with a composition of 10 %, hornblende minerals having an abrasion pH of 10 with a composition of 10 %, and quartz having an abrasion pH of 6 - 7 with a composition of 5 %.
- Andesitic lava containg pyroxene minerals having an abrasion pH of 10 with a composition of 10 %, hornblend minerals having an abrasion pH of 10 with a composition of 10 %, and quartz having an abrasion pH of 6 - 7 with a composition of 5 %.

These minerals have a major effect on the pH of abrasion. The values obtained are listed in Table 5. Calcite has an average pH of 8.87, lower than andesitic lava, but higher when compared to basaltic lava, laharic breccia, Bunder intrusion, and Cendana intrusion. The pH of the rock abrasion can be lower or higher depends on the presence of the mineral composition.

Neutralization Value

The following are the analysis results of the neutralization value (Table 6).

Table 6. Neutralization Value of Rock Samples

Rocks sample	Average neutralization (me%)	Inferred resources (kg)	Neutralizing ability (%)*	Total neutralization potensial (me)**
Basaltic lava	593,33 ± 11,55	58.464.000	26,97%	3,47 x10^{11}
Andesitic lava	426,67 ± 30,55	51.974.400	19,39%	2,22 x10^{11}
Laharic breccia	526,67 ± 11,55	50.164.800	23,94%	2,6 x10^{11}
Bunder intrusion	626,67 ± 11,55	29.439.360	28,48%	1,8 x10^{11}
Cendana intrusion	340 ± 20	41.130.360	15,45%	1,4 x10^{11}
Calcite	2200 ± 0	-	100,00%	-

(*) Calcite ability

(**) Total neutralization potensial = inferred resources x average NP x 10.000

The neutralization value of all sample rocks is below calcite, because in the sample rock there are many minerals made up of orthoclase, quartz, hypersthene, magnetite, apatite, ilmenite, and corundum. Thus, those minerals carry alkaline salts such as Ca, Mg, K found in rocks having smaller amounts, compared to calcite which has a high Ca composition.

Referring to Table 1, the results of XRF analysis on basaltic lava, laharic breccia, andesitic lava, and circle intrusions have the composition of CaO, MgO, and K_2O with differences in their respective values on each element. The element, carrying this basic salt, has a large effect on the neutralization value. The values obtained are presented in Table 6.

The lowest rock neutralization value is 340 me % or 15.45 % of the calcite ability, and the highest rock neutralization value is 626.67 me % or 28.48 % of the calcite ability. The elements that carry alkaline salts and the accumulated values of CaO, MgO, and K_2O have the same value as the results of neutralization from rocks, as follows: basaltic lava rock > laharic breccia > rounder intrusion > andesitic lava > Cendana intrusion. Based on the neutralization value, it can be concluded that it takes four to five times of the amount needed when compared to calcite to fix nutrients in highly weathered (acidic) soil. However, the advantages of rock fertilizer compared to calcite are that in addition to improve the soil pH. It also improves the other nutrients that have been partially lost in the soil.

Discussion

Based on the agrogeological potential including electrical conductivity, abrasion pH, neutralization value, and each nutrient resource, it can be concluded that the rock samples have the most potential to be used as ameliorant and fertlizer for highly weathered (acidic) soils (Ismangil, 2009).

The lowest neutralization value of the rock is 340 me % or 15.45 % for calcite ability, and the highest neutralization value of the rock is 620 me % or 28.18 %. Based on the importance of neutralization, it takes four to five times of the amount required compared to calcite to improve the soil that is already acidic or infertile. But the excess of fertilizer rocks compared to calcite, besides enhancing the soil pH, it also improves the nutrients that have been partially lost in acid soils.

On the basis of the electrical conductivity parameter, all values are non-saline which means safe for plants. The abrasion pH parameter show that all rock samples have an average pH value of 8, the neutralization values of 15.45 % - 28.48 % from the ability of calcite within the five prospect samples which act as an ameliorant. The highest ameliorant is in the basalt lava rock because basaltic lava has a large resource value for nutrients and a large neutralization value.

The research approach utilizes the principles of geochemical processes to accelerate the dissolution of nutrients in primary minerals-volcanic rocks into more readily available to plants. Thus, the process of restoring agricultural land can be done faster. This study has a weakness in the form of preparation of rock samples that are crushed to the size of clay. But the neutralization value produces a good weight, so the rock can meet the conditions as the land amendment.

Conclusions

The rock geochemistry of the studied area shows that the magmatic series belongs to the calc-akaline series. The origin of magma interacts with the continental crust and the origin of magma based on tectonic settings is in the tholeiite island-arc and island-arc calc-alkaline basalt.

Igneous rocks of Slamet Volcano in the studied area in the form of basaltic lava, andesitic lava, laharic breccia, cendana intrusion, bunder intrusion have good prospects as an ameliorant of highly weathered soil (acidic) with components which have been tested in the form of nutrients with existing content. The macro- and micro nutrients are P, K, Mg, Ca, Fe, Mn, and Si, which function as fertilizers for plant to grow.

The conductivity value classified as non-salinity is safe as soil improvement. Whilst a neutralization value relative to calcite and the pH value of abrasion is suitable for increasing the pH of highly weathered soils. The electrical conductivity parameter, indicates that all values including non-salt, and the abrasion pH parameter, all rock samples have an average pH value of 8, indicating the prospect of being the highest ameliorant in basaltic lava, because this basalt has a resource value, large in nutrients, high neutralization value, and it is the second highest (after Bunder intrusion) one.

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