The Effect of Heating, Boiling and Acidification Techniques on the Total and Exchangeable Contents of K, Ca, and Mg in Volcanic Ash of *Sinabung* of North Sumatra

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Keywords: Volcanic Ash, Heating, Boiling, Acidification.

Abstract: This research is aimed at studying the effect of heating, boiling, and acidification techniques of Sinabung Volcanic Ash (AVS) material on the total and exchangeable concentrartion of K, Ca, and Mg, to obtain a technique that can increase the exchangeable content of K, Ca, and Mg, and to produce products of agrotechnolgy containing exchangeable K, Ca, and Mg in high concentration. This experiment uses a non factorial completely randomized design. The treatments tested were 3 types of techniques consisting of: oven-heating technique of 100oC (PO), 100oC (PA) water-boiling technique, and 0.01N HCl acidification technique (US). Each treatment technique was carried out for 6 hours. The variables observed included the total content of K, Ca, and Mg (extractant ingredients H2SO4 (p) and HCl (p), and the exchangeable content of K, Ca, and Mg (NHOAc, pH 7.0), the ratio of K, Ca, and Mg to be exchangeable for the total amount, and the relative ratio between elements K, Ca, and Mg. Measurement of K, Ca and Mg elements uses the Atomic Absorption Spectrophotometer (AAS) tool. The results showed that the effect of heating technique treatment with oven 100^{o}C (PO), boiling water 100^{o}C (PA), and acidification techniques with 0.01 N HCl were significantly different in increasing total and exchangeable contents of K, Ca, and Mg, releasing rate of exchangeable contents of K,Ca, and Mg. Acidification technique is the best technique in increasing all the variables observed and manufacturing products of agrotechnology, followed by heating and boiling techniques. Three products were found and marked by codings of AVS-A0,01-6, AVS-O100-6, dan AVS-W100-6.

1 INTRODUCTION

Sinabung Mountain is one of the mountains located in Karo District of North Sumatra, Indonesia at coordinate position of 03^{o} 10’ NL and 98^{o} 23’ EL and highest peak of 2.460 m from the sea level. Historically, Sinabung Mountain has never erupted since 1600. However it is reactive and some eruptions have occured, and the first one occured on August 27, 2010.

Although Sinabung eruptions have distructed the crops, resulting bad impacts on the people in its surroundings, and high financial loss (Retnaningsih, 2013; Sudiarso, 1987), the volcanic ash produced from the Sinabung eruption is reported to be able to improve the quality of chemical and physical properties of soil (Andhika, 2011; Rostaman et al. 2011). It is also reported that Volcanic Ash of Sinabung (VAS) contains some nutrients (Sinuhaji, 2011; Barasa, 2012) and primary minerals as sources of plant nutrients (Khusrizal *et al.*2018). According to Khusrizal et.al (Khusrizal et.al. 2018), the VAS in depth of 0-24 cm contains primary minerals such as plagioclas (34%), hipersthene (9%), augite (3%), and amphibole/hornblende (5%). These minerals are sources of plant nutrients such as K, Mg, and Ca. The total contents of each element in VAS are found in the amount of 2,27 %, 8,12 %, and 2,28 % respectively. All these cations are unavailable to be absorbed by plants as they are still in mineral structures. These cations can be available to plants if the minerals have been weathered by the rections as the following:

Calsium (Ca) sources from weathering of Ca-plagiclase

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$CaAlSi_2O_8 + H_2CO_3 + ½O_2 = Al_2Si_2O_5(OH)_4 + Ca^{2+} + CO_3^{2-}$ ....(1)

Magnesium (Mg) sources from weathering of hypersthene are:
$MgFeSi_2O_3 + 2H_2CO_3 = Mg^{2+} + Fe^{2+} + 2HCO^{3-} + SiO_2 + H_2O$.......(2)

Potassium (K) sources from weathering of feldspar or orthoclase are:
$2KAlSi_3O_8 + 2H^+ + 9H_2O = HAlSi_2 + 4H_4SiO_4 + 2K^+$ .... (3)

The concentration of K, Ca, and Mg is exchangeable form and/or available to the plants depending on the reaction rate that is controlled by some factors such as mineral species, temperatures, soil acidity, and soil moisture. According to Bowen Series, the rate of weatherable minerals is deteriorated from amphibole, biotite until K-felsdpar (Bowen, 1928). Under the condition of high temperature and low pH, it could support promoting the rate of dilution process resulted from the minerals destroyed releasing exchangeable cations. Soil moistures are responsible to control hydration and reduction–oxidation process. By this process, iron (Fe) in mineral structure, and pyroxene can be reduced or oxidized so that the mineral is destroyed and some cations are released (Schott et al., 1981). All the processes are able to increase the concentration of exchangeable cations.

In order to improve the concentration of exchangeable contents of K, Ca, and Mg, the volcanic ashes can be treated by promoting the decomposition of mineral such as heating, boiling, acidification, and fermentation. All of these technique tereatments are recommended to be conducted by Khusrizal et al (Khusrizal et al. 2018).

This research aims to study the effect of heating, boiling, and acidification techniques on total and exchangeable form contents of K, Ca, and Mg, to find technique that is able to increase the exchangeable forms of K, Ca, and Mg and to produce the argotechnology product containing exchangeable forms of K, Ca, and Mg in high amount.

In addition, these products can potentially be applied to substitute or reduce the fertilizer material from other sources, such as KCl and/or dolomite ($CaMgCO_3$). Finally, it can reduce the financial budget or increases benefits in farming.

2 RESEARCH METHOD

The experiment was conducted in Laboratory of Faculty of Agriculture, Islamic University of North Sumatra. The materials of VAS were colleted in depth of 0-10 cm from Karo District, Taman Taran Sub District, Sigarang-garang village. The location is in coordinate position of $3^0$11'27.1"N 98^0 24'52.1" E. Morphologically, VAS is characterized by gray color, and used to distinguish between VAS and soil materials in its surrounding. The VAS collected was sieved by using the screener of 40 mesh in size in order to minimize the texture and homogenity of VAS materials.

The experiment was arranged in Non Factorial Randomized Complete Design. Three techniques as treatments were tested consiting of heating 100ºC by oven (PO), boiling 100ºC (PA), and acidification by HCl 0,01N (AS) techniques. ***Heating technique*** of 100º C by oven was run in accordance with the procedure in which 2 kg of VAS material was heated in 100º C in oven for 6 hours. Afterwards, the VAS material was cooled under closed room temperature, and direct blow of wind is to be avoided. After VAS material was cool, it was put in a bucket of 2 kg in capacity. This product was marked with a code as AVS-O100-6.

Boiling technique was conducted by using the procedure in which 2 kg of VAS material was boiled in 1 liter of water in 100º C for 6 hours, and stirred until turning into mud. Then, The VAS material was cooled under closed room temperature, and the direct blow of wind is to be avoided. The cooled VAS material was put into a bucket of 2 kg in capacity. This product is signed with a code as AVS-W100-6.

Acidification technique was done by the procedure in which 2 kg of VAS material was mixed with 1 liter of 0,01N HCl and stirred for 6 hours in mixer. VAS material was dried in closed room temperature for 6 hours, and then put into the bucket of 2 kg in capacity. This was marked with a code as AVS-A0,01-6

The variables observed consisted of the total concentration of K,Ca, and Mg (extracted by concentrate of $H_2SO_{4(c)}$ dan $HCl_{(c)}$), exchangeable content of K, Ca, and Mg (NH_4OAc, pH 7,0), exchangeable ratio of K,Ca, and Mg to totality of K,Ca, dan Mg, and each product of AVS-O100-6, AVS-W100-6 and AVS-A0,01-6 and VAS was standard. Both the total or exchangeable contents of K, Ca, and Mg were determined by using Atomic Absorption Spectrophotometer (AAS).

3 RESULTS AND DISCUSSION

3.1 The Effect of Heating, Boiling, and Acidification Techniques on Total Contents of K, Ca, and Mg in VAS

3.1.1 Potassium Total (K)

The effects of heating, boiling, and acidification techniques on total content of K in VAS are presented in Figure 1. Figure 1 shows that the effect of heating and boiling techniques (oven and water) and acidification technique are different significantly on the total concentration of K, Ca, and Mg in VAS. The effect of acidification technique is the highest of that of heating and boiling techniques. The latter techniques of heating and boiling are not different significatly according to DMRT test.

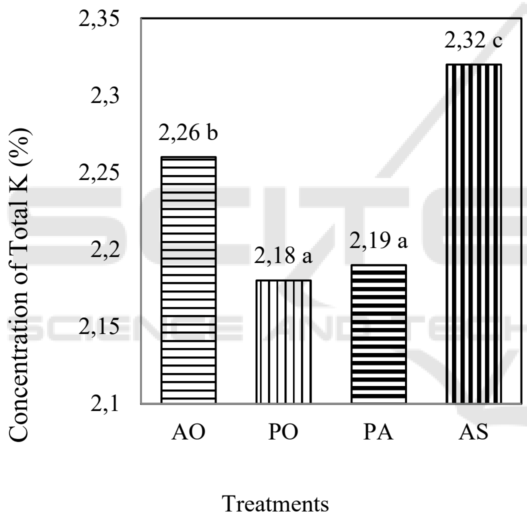

Figure 1: The Effects of Heating (PO), Boiling (PA) , and Acidification (AS) Techniques on Total content of K in VAS.

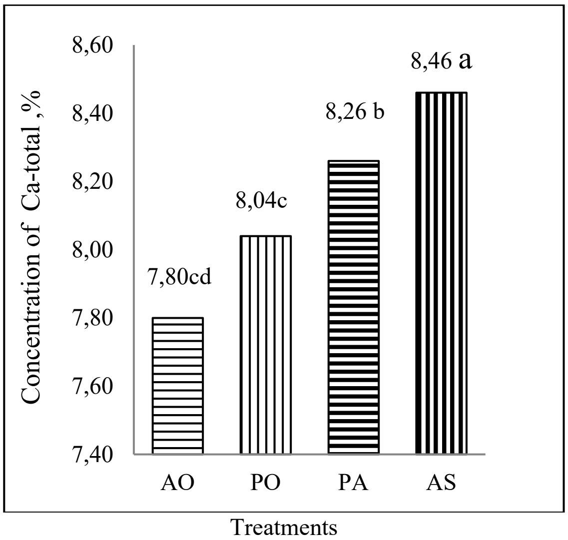

Figure 2: The Effects of Heating (PO), Boiling (PA), and Acidification (AS) Techniques on Total of Ca in VAS.

3.1.2 Calsium Total (Ca)

The effects of heating, boiling, and acidification techniques on total content of Ca in VAS are presented in Figure **2.** The effect of acidification technique is highest on the total content of Ca (8,46%) folowed by boiling technique (8,26%), and heating technique (8,04%), and controlled treatments (7,80%).

3.1.3 Magnesium Total (Mg)

The effects of heating, boiling, and acidification techniques on total of Ca in VAS are presented in Figure 3**.**

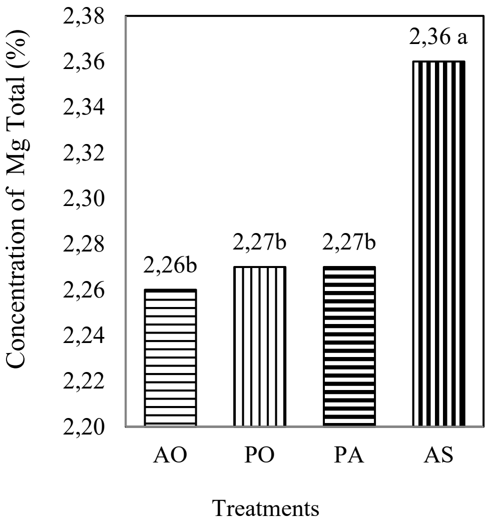

Figure 3: The Effects of Heating (PO), Boiling (PA), and Acidification (AS) Techniques on Total of Ca in VAS.

Figure 3 shows that the effects of the techniques are significantly different on concentration of total of Mg. Acidification techniques produce highest concentration of total of Mg followed by boiling (2,27%), heating technique (2,27%), and VAS as standard tereatment (2,26%). Both the techniques, boiling and heating are not significanly different.

Acidification technique produces highest concentration of total of K, Ca, and Mg, and it can be caused by some alternative reasons such as: (1) acidification reaction involved is responsible in weathering of minerals as representive in weathering reaction of *Ca-plagioklas* (equation 1), *hipersten* (equation 2), and *feldspar/orthoklas* (equation 3) in naturally weak acid (H_2CO_3) (Scott et al 1998); (2) in acidification technique there are double acidification treatments, both of which are by HCl 0.01N and in extraction using the mixed hard acids (H_2SO_4 and HCl). This action can possibly destroy the minerals in big amount so that Ca should be released; and (4) under natural condition, the weathering of minerals involves carbonate acid. (H_2CO_3) is weak acid; while in application of acidification technique, the hard acid (HCl) is used.

Environment under control by hard acid can support to accelarate the reaction rate to improve weathering of mineral intensively and dialution of K, Ca, and Mg could be exchangeable increasing the concentration.

3.2 The Effect of Heating, Boiling, and Acidification Techniques on Exchangeable Contents of K, Ca, and Mg in VAS

3.2.1 Exchangeable Content of K

The effects of heating, boiling, and acidification techniques on exchangeable content of K in VAS are significantly different as presented in Figure 4**.** Figure 4 shows that the concentration of exchangeable content of K is treated by acidification technique of the highest of (2,01 me%), and then the heating is decreased to (1,77 me%) and (1,72 me%) and AVS is standard (1,70 me%) respectively.

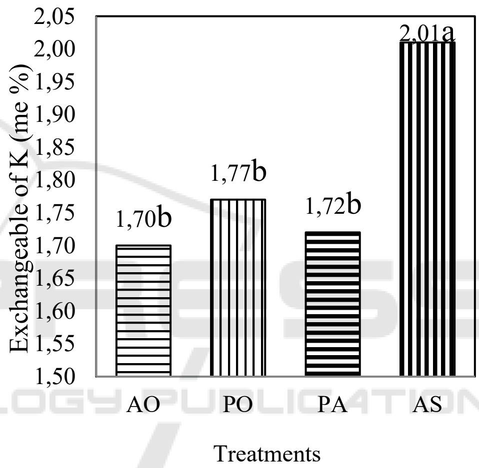

Figure 4: The Effect of Heating (PO), Boiling (PA) , and Acidification (AS) Techniques on Exchangeable content of K in VAS.

3.2.2 Exchangeable Content of Ca

The effects of heating, boiling, and acidification techniques on exchangeable content of Ca in VAS are presented in Figure 5**.** The Figure 5 shows that the exchangeable concentration of Ca in VAS that are treated by heating, boiling, and acidification techniques produce 21,7 me%, 21,46 me%, and 21,8 me% respectively. All the techniques are not significantly different, but they are significantly different from the standard treatment (20,45 me%).

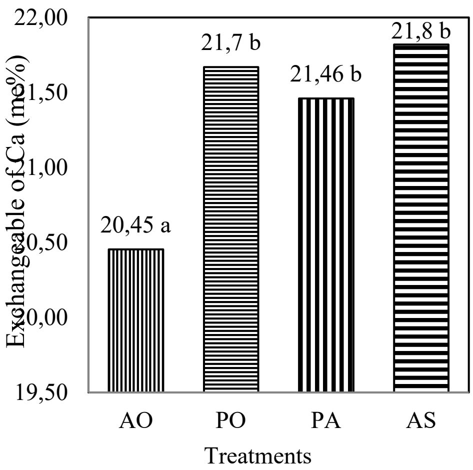

Figure 5: The Effects of Heating (PO), Boiling (PA), and Acidification (AS) Techniques on Exchangeable Content of Ca in VAS.

3.2.3 Exchangeable Content of Mg

The effects of heating, boiling, and acidification techniques on exchangeable content of Mg in VAS are presented in Figure 6**.** Figure 6 shows that heating and boiling techniques are not different, but signifiacantly different with acidifiacation techniques in producing the concentration of exchangeable content of Mg. Acidification technique produces the highest exchangeable concentration of Mg, and decreases in heating (8,41 me%), boiling (8,34 me%), and AVS is in standard treatment (8,18 me%).

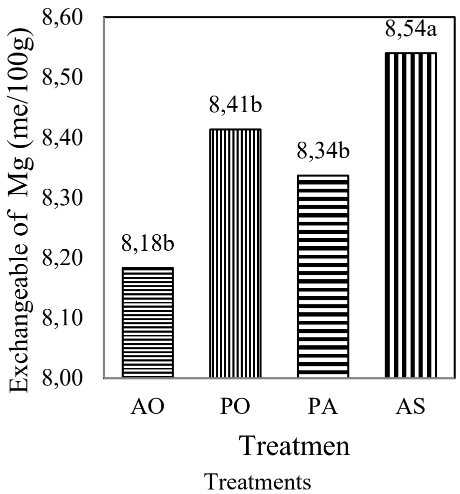

Figure 6: The Effect of Heating (PO), Boiling (PA) , and Acidification (AS) Techniques on Exchangeable Content of Ca in VAS.

Treatment by using acidification technique produces significantly the highest exchangeable concentration of K and Mg compared to Ca. This fact can be caused by some possible reasons such as: (1) acidification is able to distruct directly the mineral structure by reaction with elements in meneral structure and release K,Ca, and Mg to be exchangeble form or available to plant. (2) meanwhile, both heating and boiling techniques only occur in the addition of heat energy, and indirectly react with elements in mineral structure with lower result in releasing K,Ca, and Mg in exchangeable form; (3) duration of heating and boiling for 6 hours is not enough to optimalize to destruct or dilute the primer minerals and release the exchangeable forms of K,Ca, and Mg. But, both of the techniques have the ability to produce the exchangeable forms of K, Ca, and Mg higher than standard treatment or control of VAS. On the other hand, all of the techniques have potential ability to increase or release the exchangeable concentration of K, Ca, and Mg or available to plant.

3.3 Rates of K,Ca, and Mg Release

Release of K,Ca, and Mg is an exchangeable form due to destruction of mineral structure resulted from the treatment of heating, boiling, and acidification techniques. The exchangeable contents of K, Ca, and Mg are available form that can be absorbed by plant roots. Rate of K,Ca,and Mg release can be predicted base on the exchangeable ratio to total form of K, Ca, and Mg. The ratio value is presented in Figure 7, 8, and 9. Figur 7 and 9 show that the rate of release of the exchangeable contents of K and Mg are significantly different. The highest concentrations of K and Mg are found in treatment of acidification technique and decreased in boiling technique and heating respectively (Figure 7). Meanwhile, rate of Ca release is also significantly different and highest concentration is found in treatment of boiling technique, but there is no difference to all other treatments (AO, PO, and AS) (Figure 8).

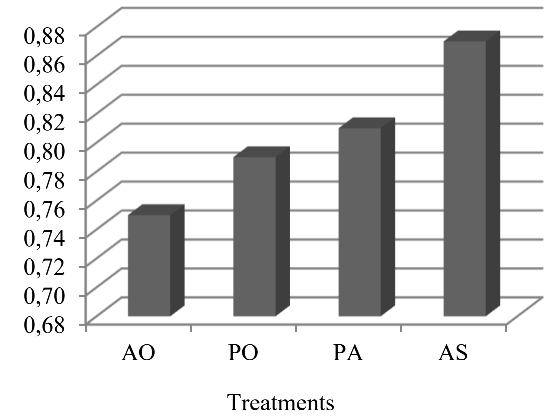

Figure 7: The Effect of Heating (PO), Boiling (PA), and Acidification (AS) Techniques on Ratio of K-exch./K-total in VAS.

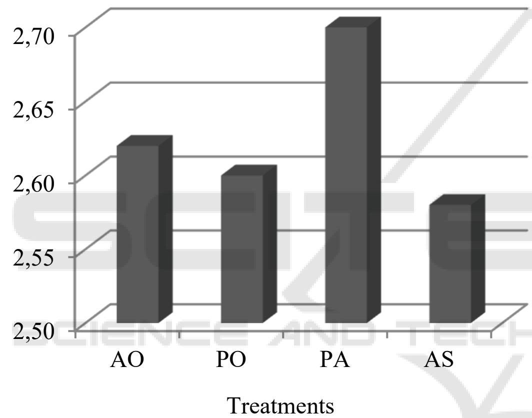

Figure 8: The Effect of Heating (PO), Boiling (PA) , and Acidification (AS) Techniques on Ratio of Ca-exch./Ca-total in VAS.

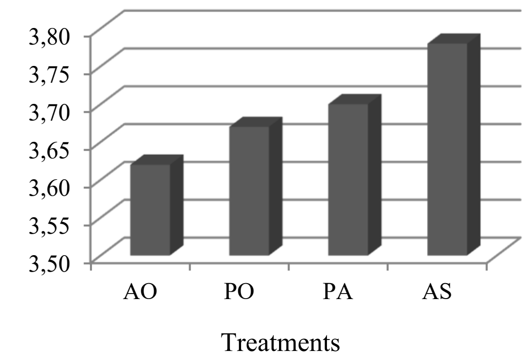

Figure 9: The Effect of Heating (PO), Boiling (PA) , and Acidification (AS) Techniques on Ratio of Mg-exch./Mg-total in VAS.

3.4 Relative Rate of Release for Exchangeable Contents of K,Ca, and Mg

Relative rate of release for exchangeable contents of K,Ca, and Mg can be explained based on ratio of the exchangeable concentration to total concentration of K,Ca, and Mg. Based on the ratio, relative rate of release of K,Ca, and Mg shows significant difference in all treatments as presented in Figure 10. The figure also shows that the relative rate of release between elements of K, Ca, and Mg in all of treatments are different significantly. Relative rate of release for Mg is highest and decreased for Ca and K (Mg>Ca> K) and in standard treatment respectively.

The highest release for Mg is possibly correlated with source of Mg originating from hipersthene that contains Fe in its structure. Hypersthene belongs to mineral of ferromagnesian group. It is relatively weathering minerals due to exchanges of Fe^{3+} (ferri) to Fe^{2+} (fero) resulted from the influence of reduction-oxidation condition and low stage in pH (VAS pH, more or less 4.0). Under this condition this can facilitate or support the weathering of hipersthene efectively and release Mg to be exchangeable form faster than those of K and Ca. Both of the elements, K and Ca, are sourced from felspar/orthoclase and plagioclase. These minerals do not have Fe in their structure resulted from the weathering that may occur in relative lower stage so that the release rate of the element becomes exchangable form, also relatively low.

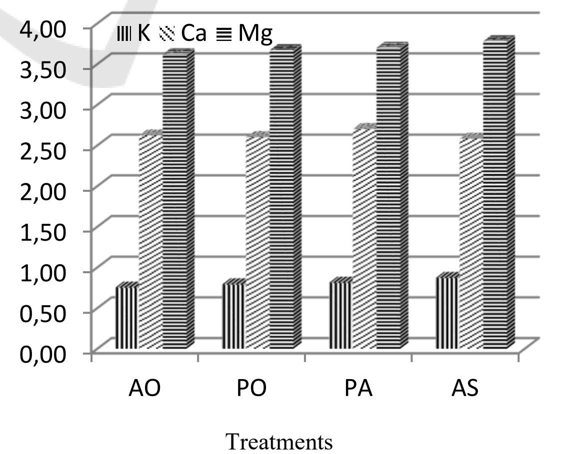

Figure 10: The Effect of Heating (PO), Boiling (PA) , and Acidification (AS) Techniques on Ratio of K-exch/K-total,Ca-exch/Ca-total, dan Mg-exch/Mg-total AVS.

4 CONCLUSIONS

1. The effects of heating by oven at 100 ^{o}C, boiling at 100 ^{o}C, and acidification techniques are different significantly and could increase the total and exchangeable concentration, and release rate of K, Ca, and Mg
2. The effect of acidification technique is highest in producing the total and exchangeble concentration of and in improving the release rate of K, Ca, and Mg and decreased for heating and boiling techniques respectively.
3. The acidification is the best technique and can be potentially used to manufacture VAS, useful as a soil amendment product in future.
4. The best product based on exchangeable concentration of K,Ca, and Mg or available form is produced by acidification technique and folowed by heating and boiling techniques.
5. Each product is marked by the coding as AVS-A.01-6, AVS-O100-6, and AVS-W100-6 respectively.

5 RECOMMENDATION

Exchangeable concentration of K,Ca, and Mg are still relatively low compared to total concentration. All products produced above can potentially be used in agrotechnology, but need to be tested in order to impove all the existing techniques.

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