Enhancing the Solubility of Indrapuri Clay (Local "Kieserite"Fertilizer)

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Abstract. Study on enhancing the solubility of clay containing magnesium of local production (Indrapuri) has been conducted. The clay is commercially available and named as "kieserite" produced by local companies. The sample was taken randomly from fertilizer shops and analysed with AAS and XRF methods. XRF data of local kieserite showed the dominated chemical content; $MgO(33.19\%)$; $SiO_2(33.11\%)$; $CaO(1.90\%)$;Al_2O_3 (5.77%) and $Fe_2O_3(6.32\%)$. The MgO content is higher than that of magnesium sulphate monohydrate **(**CAS No.: 14168-73-1) which is only 28%. The concentration of soluble magnesium ions of local kieserite naturally soluble was 0.0186% which is very low compared with the soluble magnesium of magnesium sulphate monohydrate **(**CAS No.: 14168-73-1) which is 25%. The Enhancing the magnesium solubility was done by soaking the local kieseriteinto 0.1-0.5M HNO_3 before neutralized with NH_4OH or mixing the local kieserite with in alluvial, entisol, red-yellow-podsolik (RYP) soils with and without addition of 0.1-0.5M of $(NH_4)_2SO_4$. The amount of dissolved magnesium of kieserite was found more in entisol soil than the other type of soils. The concentration increased up between 0.59-1.00% along with the incrementof $(NH_4)_2SO_4$ concentration (0.1-0.5 M). Both in entisol soil and in 0.1 M of $(NH_4)_2SO_4$, the dissolved magnesium ion increased up to 0.825% but decreased at higher concentration of $(NH_4)_2SO_4$.
Keywords: Kieserite, solubility, magnesium, fertilizer

Introduction

Magnesium is one of minor nutrients but essential for plants nutrient (Mikkelsen, 2010) and acts as the central element of chlorophyll, the molecules involve in photosynthesis. Plant absorbs magnesium ion from clay and compost. However most of magnesium resources are insoluble in water therefore the magnesium uptake by plants often very low. Previous research showed that increasing magnesium in tea leaf brought to higher tea production (Yuwono *et al.*, 2002; Jayaganesh *et al.*, 2011). The crude protein of grass (*P. maximum* (*var*Ntchisi) treated with unhydrous magnesium sulphate fertilizer was consistently higher than then untreated ones (Fajemilehin *et al.*, 2008). Most of magnesium compound is insoluble in water except the sulphate, chloride and nitrate compounds. Source of magnesium is dolomite, lime along with compost and manures. Magnesium fertilizer is usually in form epsomsalt ($MgSO_4.7H_2O$: 9.6 % Mg), kieserite ($MgSO_4.H_2O$: 18.3 % Mg), dolomite ($MgCO_3.CaCO_3$: 5-20 % Mg) andmagnesite ($MgCO_3$: 45% Mg) (Mikkelsen, 2010). Kieserite ($MgSO_4.H_2O$) that is known as a magnesium fertilizeris slowly soluble in water where a synthetic magnesium sulphate (SMS) ismagnesium fertilizer that immediately soluble in water (Härdter et al, 2005).

Many fertilizer companies claimed that clay containing magnesium is kieserite.Clay naturally is insoluble in water and study on the solubility and interaction with other fertilizer hasbeen reported previously (Härdter *et al.*, 2005; Rheinbaben., 1986; Jones *et al.*, 2009). Several local companiesin Aceh province produce clay containing magnesium as a fertilizer naming as "kieserite" mined from KecamatanIndrapuri, Aceh Besar Province, Indonesia. This product is commercially available in form of pellets and it is not crystallite $MgSO_4$. Although the MgO content has been claimed to be 28-30% and full-fill the Indonesian national-standard industry, the amount of soluble magnesium ions that are readily

absorbed by plant might not as much as the MgO. Thereby study on the enhancing the solubility of the local kieserite is crucial to improve the effectiveness of the fertilizer and to give information for the fertilizer customers.

Materials and Methods

Determination of total magnesium content

UsingX-Ray Fluorescence (XRF)

Amount of 5 kg sample of local magnesium fertilizer with brand name of "Pupuk Kieserite Super cap Sawit" produced X company located at KM 16,2SibreKeumudeIndrapuri Aceh Besar, was taken from the factory. The sample was air dried and mixed truly before it was divided five portions. Approximately 100 g of the portion was sent to geology laboratory located at Jl. Deponegoro No. 57 Bandung, 40122 Indonesia for XRF analysis as common practiced in for mineral analysis that available in literature (Ramli *et al.*, 2011).

Using Atomic Adsorption Spectroscopy (AAS)

Amount of 2.12 g dried local kieserite samples was destructed by addition a few drops of aqua regia till the sample dissolved. Then the mixture was evaporated by heating slowly but avoided being boiled. The dried residue was diluted with distilled water and carefully transferred into 25 ml of volumetric flask and added distilled water up to 25 ml. Amount of 2.5 ml was pipetted and diluted to 250 ml volumetric flask. This solution was pipette 25 ml and diluted into 250 ml in separated volumetric glass before AAS analysis. The magnesium standard solution for AAS was prepared in 0.01; 0.05; 0.10 and 0.15 ppm. Magnesium content was determined from the absorbancesubstituted in calibration curve standard.

Determination of soluble magnesium ions

Amount of 200 g sample was placed in oven at $110^{\circ}C$ for several yours and frequently weighted until the constant weight. A portion of 50 g local kieserite was soaked in 500 ml of distillated water and stirred for a week. Everyday the supernatant was pipetted and filtered to take 25 ml of the solution for determination of soluble magnesium ion concentration by AAS methods.

The effect of soil type environment and the magnesium ions solubility

Each portion of local kieserite (50 g) was mixed with alluvial, entisol, red-yellow-podsolik (RYP) soils and the weights of each type soils were 50 g, 150 g and 200 g and added 500 ml distillated water and stirred for a month. The characterized soils were obtained from Soil Lab of Syiah Kuala University. Each mixtures was stirred for 6 h a week before sampled and filtered to take 25 ml of the supernatant for soluble magnesium ion determinations by AAS methods.

The effect of $(NH_4)_2SO_4$ on the magnesium ion solubility

In separated experiment, 10 g of dried local kieserite was soaked in 500 ml of 0.1; 0.3; and 0.5 M of $(NH_4)_2SO_4$ and stirred for a week. The mixture was settled down and pipetted 25 ml of the supernatant for soluble magnesium determinations by AAS methods. Then, the experiment was repeated by addition 20 g of entisol soil into the mixture and sampling for soluble magnesium determination.

Results and Discussion

Determination of metal content of soil type material like kieserite by using X-Ray Fluorescence (XRF) is common in geology sample analysis. XRD is non-destructive method and it can be carried out very fast compared with the common chemical analysis methods. The chemical content of sample was analysed in dried and solid material and the X-ray reflection of the atoms was compared with diffract gram of the known chemicals that have been recorded as file in the library data. Using this method the chemical composition of local kieseriteis tabulated in Table 1.

The total magnesium content

The local kieserite was composed mainly by silica (33.11%) and magnesium oxide (33.190%) and some other compounds as shown in Table 1. The magnesium metal was 20.020%. This data indicated that local kieserite is much higher magnesium contents than other commercial magnesium fertilizer and full-fill the industrial national standard. Should this method reliable then magnesium content of kieserite is much higher the pure and

water-soluble compound of $MgSO_4.H_2O$ which is the magnesium content is only 18.3 % (Mikkelsen, 2010). In fact the local kieserite is hardly soluble in water therefore the soluble magnesium is not as high as the XRF data. Due to its low solubility in water this "the local kieserite" is different from the known soluble kieserite (SMS). The accuracy of XRF measurement is still debatable especially on its limitation to measure the abundance of main elements since the measurement was affected by the wavelength and the intensity of incident x-rays (*www.ci.stamford.ct.us/.../XRFMeasurements.p*.). However this data seems to be the only resource data to just the magnesium of local kieserite for the selling permit.

Table 1. The main chemical composition of local kieserite based on XRF data.

Oxides	Amount(%)	Elements	Amount(%)	SD
SiO_2	33.110	Si	-	0.240
MgO	33.190	Mg	20.020	0.140
LOI	18.420	-	-	-
Fe_fO_3	6.320	Fe	4.040	0.090
Al_2O_3	5.770	Al	3.050	0.060
CaO	1.900	Ca	1.360	0.050
As_2O_3	0.390	As	0.300	0.020
Cr_2O_3	0.270	Cr	0.300	0.020
NiO	0.220	Ni	0.172	0.090
Cs_2O	0.100	Cs	0.095	0.035
MnO	0.099	Mn	0.076	0.004
Rb_2O	0.050	Rb	0.046	0.003
TiO_2	0.037	Ti	0.022	0.011
CuO	0.010	Cu	0.008	0.003

Therefore the total magnesium content was further analysed by Atomic Adsorption Spectroscopy (AAS) which widely used in chemical analysis. In this method, the sample was destructed by aqua reqia so that all magnesium was forced to dissolve in acid and diluted with distillated water. The instrument was calibrated with magnesium standard solution and the finding is listed in Table 2. The magnesium content was only average of 7.4% which is much lower than those in XRF data. This data seems to be more reliable since the local kieserite was insoluble in water and not purely composed of magnesium sulphate. The difference between XRF and AAS data is due to different accuracy (*www.clu-in.org;*Shefsky, 2007*).*

Table 2.Magnesium content of local kieserite.

Sample weight (g)	Mg (g)		Mg(%)
2.12	0.1664		7.85
2.12	0.1599		7.54
2.12	0.1485		7.00
		Mean	7.40

The dissolved magnesium ions from local kieserite

After soaking the local kieserite in water for four weeks with stirring, the filtrate was analysed to determine the soluble magnesium ions. The supernatant was pipetted and filtrated than the filtrate was analysed with AAS methods. It was found that the soluble magnesium ions were 0.069% which is very low compared to the total magnesium contents. The soluble magnesium ion concentration was not significantly increase after week by week for one month. This indicated that the magnesium compound in local kieserite is insoluble in water and it might not dominated by magnesium sulphate which has high solubility in water. As comparison, the relatively pure magnesium sulphate monohydrate ($MgSO_4.H_2O$) with CAS No: 14168-73-1 that has also known as truly kieserite releases water-soluble magnesium up to 25%. Therefore local kieserite fertilizer will release very low magnesium ions for the plant to be absorbed since the plant absorbs mineral that

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dissolved in water (Argo, 2003; Novizan, 2005; Dwidjoseputro, 1994). The presence of magnesium oxide as recorded the main compound in the XRF data was not match characteristic with its pH of solution that observed as neutral solution. Should the local kieserite composed of MgO then the pH solution should be basic since MgO will react with water to form $Mg(OH)_2$ but this not happen. Therefore although the total magnesium content was considered high based on XRF data, the amount of soluble magnesium ions that can be absorbed by plant is very low.

The effect of soil type environment and the magnesium ions solubility

The three type of characterized soils; alluvial, entisol, red-yellow-podsolik (RYP) was obtained from soil laboratory of agriculture faculty, Syiah Kuala University. Among the characterized parameters, pH and Cation exchange capacity (CXC) were the most various in the soil samples as displayed in Table 3.

The naturally dissolved magnesium in the soil samples was lower than in local kieserite which is 0.069% as shown in Table 3. Among the soil, entisol has the highest dissolved magnesium and RYP was the lowest. Should it is referred to its soil pH, apparently that the higher pH tend to have more dissolved magnesium. Novizan (2005) said that pH of 6.0-7.5 is the ideal pH for metal ions being available to be absorbed by the plants.

When local kieserite was mixed with the soil and determined the soluble magnesium ions both with calculation that is the sum of magnesium ions from kieserite and from the soil and by analysis using AAS as described in Table 4. The highest dissolved magnesium in three soil samples was in entisol followed with aluvial and RYP soils.

The filtrate contained less soluble magnesium ion that as expected. This suggested that some of the magnesium ions bind strongly to the soil or to kieserite or both and did not leach into the water. Colloidal soil usually has negative charge that can bind cation such as Ca^{2+}, H^+, Mg^{2+}, K^+, Na^+, Al^{3+} and NH_4^+. The cation bind to the colloid will not easily leach and run off into the water (Novizan, 2005; Tan, 1991).

Table 3. Typical characteristic of soil samples

Parameters	Alluvial	Entisol	Red-Yellow-Podsolik (RYP)
pH	6.02	7.62	5.53
CEC (me /100 g)	8.60	16.80	10.8
Dissolved magnesium (%)	0.017	0.03	0.003

Table 4. Dissolved magnesium subject to interaction between kieserite and soil samples.

Samples	Dissolved magnesium ions		
	Calculation (%)	Analysis (%)	Absorbed by soil (%)
100 g Entisol + 50 g of kieserite	0.1658	0.0310	0.1348
100 g Aluvial + 50 g of kieserite	0.1220	0.0230	0.0990
100 g RYP + 50 g of kieserite	0.0508	0.0140	0.0368

Entisol absorbed magnesium ions more than other soil might be as the effect of its pH of 7.62 and Cation Exchange Capacity (CEC) which was higher than other soil. When the pH more than 7 then ion OH^- might be present and reacted with Mg^{2+} to form $Mg(OH)_2$ that very low solubility in water. The higher CEC the more magnesium ions exchanged with alkali or other soluble ions.

Other experiment was carried out to see weather kieserite itself also absorbed magnesium ions. Amount of 10 g local kieserite was added into 0.01 M of $MgSO_4$ and stirred for 6 hours. Then the filtrate was analyzed for dissolved magnesium ion determination. We found that the amount of magnesium ions decreased because it was absorbed by local kieserite as presented in Table 5.

Table 5. Dissolved magnesium from $MgSO_4$ with and without kieserite environment.

Samples	Dissolved magnesium (%)
0.01 M $MgSO_4$	0.27
0.01 M $MgSO_4$ + Kieserite	0.26

The effect of $(NH_4)_2SO_4$ on the magnesium ion solubility

Interaction among local kieserite with other fertilizer and soil affecting the magnesium solubility was simulated in laboratory. $(NH_4)_2SO_4$ was used an imitating fertilizer for source of nitrogen and sulfur and it was mixed with local kieserite. The local kieserite was stirred in various concentration of $(NH_4)_2SO_4$ solution for a week and the solution was sampled periodically to determine the dissolved magnesium ions. There was no significant increment of magnesium ion after 24 hours stirring. The percentage of magnesium ions dissolved in water increase with the increase of $(NH_4)_2SO_4$ solution concentration as shown in Table 6. The increment of dissolved magnesium ions might correlate the pH decreasing as tabulated in Table 6. Decreasing pH was as a result ofhydrolyzing $(NH_4)_2SO_4$ in water and cation exchange where NH_4^+ was replaced by Mg^{2+} ions from kieserite. Then Mg^{2+} ions were balanced by SO_4^{2-} ions that are dissolved easily in water. Hydrolysis process $(NH_4)_2SO_4$ contributed H^+ that make pH of the solution decrease as presented in this reaction.
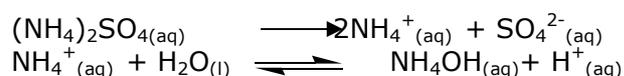
$$(NH_4)_2SO_{4(aq)} \longrightarrow 2NH_4^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$
$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+{}_{(aq)}$$

Table 6. Dissolved magnesium ions and the pH of local Kieserite in $(NH_4)_2SO_4$ solution.

No	[$(NH_4)_2SO_4$] (M)	pH	Dissolved Mg ions (%)
1	0.1	6	0.590
2	0.3	5	0.920
3	0.5	4	1.005

After the effect of $(NH_4)_2SO_4$ solution on magnesium solubility was confirmed then the next experiment was on the effect of both $(NH_4)_2SO_4$ and entisol soil. It was found that dissolved magnesium ions decreased with increasing of $(NH_4)_2SO_4$ as tabulated in Table 7. At concentration at of 0.1 M of $(NH_4)_2SO_4$ the percentage of dissolved magnesium increases from 0.590% (without entisol) up to 0.8525% (with the presence of entisol). However when the concentration of $(NH_4)_2SO_4$ was increased along with decreasing the pH, the dissolved magnesium decreased 0.507%. This apparently was due to the optimum pH for entisol to absorbed magnesium ions so that became less available in solution. However for 0.1 M of $(NH_4)_2SO_4$ and entisol condition, the dissolved magnesium ions was the highest compared to those without $(NH_4)_2SO_4$ and without entisol soil environment as described in Fig. 1

Table 7.Dissolved magnesium of local kieserite in $(NH_4)_2SO_4$ and entisol soil environment.

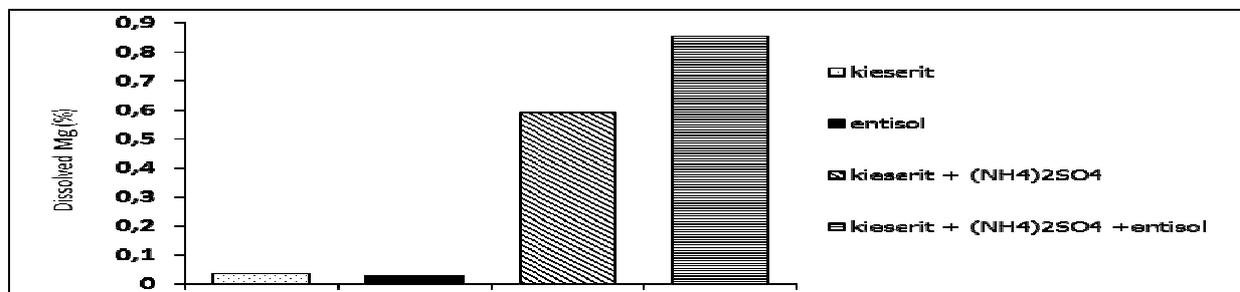| No	$[(NH_4)_2SO_4]$ (M)	Dissolved Mg ions (%)
1	0.1	0.852
2	0.3	0.577
3	0.5	0.507

Figure1.Comparison of dissolved magnesium ions from local kieserite in various environments.

Conclusions

Although total magnesium content of local kieserite was 33.19 % (as MgO) and 20.02 (as Mg), the present of dissolved magnesium in water naturally was only 0.0186%. The dissolved magnesium ions increased up to 0.0310 % in entisol soil but slightly decreased in RYP soil. However the presence $(NH_4)_2SO_4$, the concentration and type soil affect the amount of dissolved magnesium of local kieserite ions in water.

Acknowledgements

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