

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

¹Adlim, ¹Zarlaida Fitri, ¹Sulastri, ²Ratu Fazlia Inda Rahmayani,
²Yuliza Laini

¹Chemistry Department, Teacher Training & Education Faculty, Syiah Kuala University, Darussalam, Banda Aceh 23111; ²Undergraduate Student of Chemistry Department, Teacher Training & Education Faculty Syiah Kuala University, Darussalam Banda Aceh 23111; Corresponding Author: adlimbandang@yahoo.com; adlim@unsyiah.ac.id

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%); SiO₂(33.11%); CaO(1.90%); Al₂O₃ (5.77%) and Fe₂O₃(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 kieserite into 0.1-0.5M HNO₃ before neutralized with NH₄OH or mixing the local kieserite with in alluvial, entisol, red-yellow-podsolik (RYP) soils with and without addition of 0.1-0.5M of (NH₄)₂SO₄. 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 increment of (NH₄)₂SO₄ concentration (0.1-0.5 M). Both in entisol soil and in 0.1 M of (NH₄)₂SO₄, the dissolved magnesium ion increased up to 0.825% but decreased at higher concentration of (NH₄)₂SO₄.

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* (varNtchisi) treated with anhydrous 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 (MgSO₄·7H₂O: 9.6 % Mg), kieserite (MgSO₄·H₂O: 18.3 % Mg), dolomite (MgCO₃·CaCO₃: 5-20 % Mg) and magnesite (MgCO₃: 45% Mg) (Mikkelsen, 2010). Kieserite (MgSO₄·H₂O) that is known as a magnesium fertilizer is slowly soluble in water where a synthetic magnesium sulphate (SMS) is magnesium 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 has been reported previously (Härdter *et al.*, 2005; Rheinbaben., 1986; Jones *et al.*, 2009). Several local companies in Aceh province produce clay containing magnesium as a fertilizer naming as "kieserite" mined from Kecamatan Indrapuri, Aceh Besar Province, Indonesia. This product is commercially available in form of pellets and it is not crystallite MgSO₄. 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

Using X-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 16,2 Sibre Keumude Indrapuri 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 absorbances substituted in calibration curve standard.

Determination of soluble magnesium ions

Amount of 200 g sample was placed in oven at 110°C for several yours and frequently weighted until the constant weight. A portion of 50 g local kieserite was soaked in 500 ml of distilled 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 distilled 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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 kieserite is 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 $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ 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_2O_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 regia so that all magnesium was forced to dissolve in acid and diluted with distilled 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; Shesky, 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 ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) 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

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 MgSO₄ 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 MgSO₄ 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 (NH₄)₂SO₄ on the magnesium ion solubility

Interaction among local kieserite with other fertilizer and soil affecting the magnesium solubility was simulated in laboratory. (NH₄)₂SO₄ 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 (NH₄)₂SO₄ 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 (NH₄)₂SO₄ 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 of hydrolyzing (NH₄)₂SO₄ in water and cation exchange where NH₄⁺ was replaced by Mg²⁺ ions from kieserite. Then Mg²⁺ ions were balanced by SO₄²⁻ ions that are dissolved easily in water. Hydrolysis process (NH₄)₂SO₄ contributed H⁺ that make pH of the solution decrease as presented in this reaction.

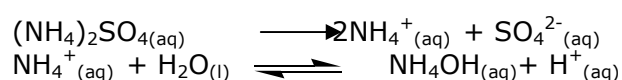


Table 6. Dissolved magnesium ions and the pH of local Kieserite in (NH₄)₂SO₄ solution.

| No | [(NH ₄) ₂ SO 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 (NH₄)₂SO₄ solution on magnesium solubility was confirmed then the next experiment was on the effect of both (NH₄)₂SO₄ and entisol soil. It was found that dissolved magnesium ions decreased with increasing of (NH₄)₂SO₄ as tabulated in Table 7. At concentration at of 0.1 M of (NH₄)₂SO₄ 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 (NH₄)₂SO₄ 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 (NH₄)₂SO₄ and entisol condition, the dissolved magnesium ions was the highest compared to those without (NH₄)₂SO₄ and without entisol soil environment as described in Fig. 1

Table 7. Dissolved magnesium of local kieserite in $(\text{NH}_4)_2\text{SO}_4$ and entisol soil environment.

| No | $[(\text{NH}_4)_2\text{SO}_4]$ (M) | Dissolved Mg ions (%) |
|----|------------------------------------|-----------------------|
| 1 | 0.1 | 0.852 |
| 2 | 0.3 | 0.577 |
| 3 | 0.5 | 0.507 |

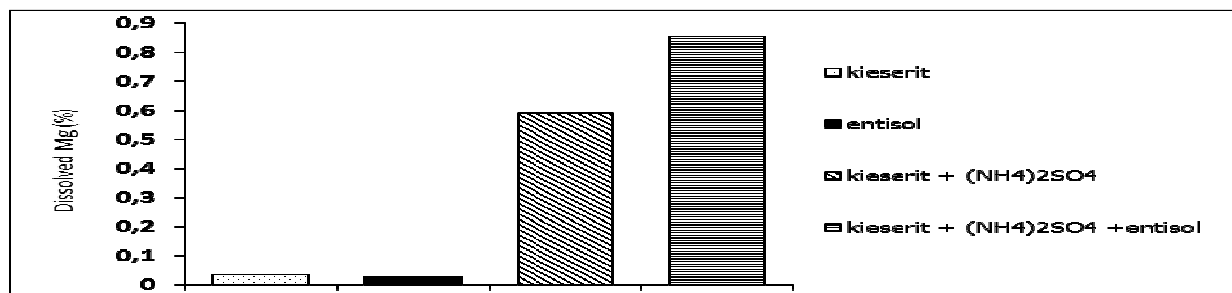


Figure1. Comparison of dissolved magnesium ions from local kieserite in various environments.

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 $(\text{NH}_4)_2\text{SO}_4$, the concentration and type soil affect the amount of dissolved magnesium of local kieserite ions in water.

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References

- Argo B. 2003. Understanding pH management and plant nutrition Part 3: Fertilizers. Blackmore Company. Originally printed in 2003 in the Journal of the International Phalaenopsis Alliance, Vol.13(2).
- Fajemilehin S.O.K., Babayemi O.J., Fagbuaro¹, S.S. 2008. Effect of anhydrous magnesium sulphate fertilizer and cutting frequency on yield and chemical composition of *Panicum maximum*. African Journal of Biotechnology, 7:907-911.
- A. Härdter R., Rex M., Orlovius K. 2005. Effects of different Mg fertilizer sources on the magnesium availability in soils. Journal Nutrient Cycling in Agro ecosystems, 70: 249-259. DOI:10.1007/s10705-004-0408-7.
- Jayaganesh S., Venkatesan S., Senthurpandian V.K. 2011. Impact of Difference Souces and doses of magnesium fertilizer on biochemical constituents and quality parameters of Black Tea. Asian Journal of Biochemistry, 6:273-281.
- Jones M.W., Papangelakis V.G., Steyl J.D.T. 2009. Kieserite Solubility in the Aqueous $\text{FeCl}_3 + \text{MgCl}_2 + \text{HCl}$ System between (338 and 378) K, J. Chem. Eng. Data, 54: 1986-1990. DOI: 10.1021/jc800735h.
- B. Mikkelsen B. 2010. Soil and Fertilizer Magnesium. Better Crops, 94:26-28.
- Novizan. 2005. Petunjuk Pemupukan Efektif. Agro Media Pustaka, Jakarta.
- Ramli Z., Rahman N.H.S.N.A., Jusoh A., Sauman Y. 2011. X-Ray Diffraction and X-Ray Fluorescent Analyses of Prehistoric Pottery Shards from Ulu Kelantan. American Journal of Applied Sciences 8:1337-1342.
- Rheinbaben W.V. 1986. Effect of magnesium sulphate addition to urea on nitrogen loss due to ammonia volatilization. Nutrient Cycling in Agro ecosystems, 11:149-159, DOI: 10.1007/BF01051058.

- Shelfsky S. 2007. Comparing Field Portable X-Ray Fluorescence (XRF) To Laboratory Analysis of Heavy Metals in Soil. The Proceeding of International Symposium of Field Screening Methods for Hazardous Wastes and Toxic Chemicals. January 29-31. Las Vegas, Nevada, USA.
- Tan H. 1991. Dasar-Dasar Kimia Tanah. Universitas Gadjah Mada. Yogyakarta.
- Yuwono N.W., Syukur A., Nurudin M. 2002. Kecukupan hara Cadan Mg di kebun teh ptagilaran. Jurnal Ilmu Tanah dan Lingkungan, 3:16-24.
- www.clu-in.org (Accessed Sept 1, 2012)
- www.ci.stamford.ct.us/.../XRFMeasurements.p. (Accessed Sept 1, 2012)