CHEMICAL CHARACTERISTICS OF ACID SULFATE SOILS AS AFFECTED BY ADDITION OF CALCIUM SILICATE IN-COMBINATION WITH AND/OR WITHOUT GROUND MAGNESIUM LIMESTONE (GML)

Short title: Calcium silicate and ground magnesium limestone alleviate soil acidity

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ABSTRACT

This study was conducted to evaluate the integral effect of ground magnesium limestone (GML) and calcium silicate on acid sulfate soils in Malaysia and to determine the optimal combination of GML and calcium silicate, with consideration on the cost incurred by the farmers and the positive soil chemical characteristics improvement on acid sulfate soil. The acid sulfate soils were incubated under the submerged condition for 120 days with GML (0, 2, 4, 6 t ha^{-1}) in combination with calcium silicate (0, 1, 2, 3 t ha^{-1}). A total of 9 out of 16 combination rates met the desired requirement of chemical soil characteristics. The chemical soil characteristics are soil pH > 4, exchangeable Al < 2 $cmol_c$ kg^{-1}, exchangeable Ca > 2 $cmol_c$ kg^{-1}, exchangeable Mg > 1 $cmol_c$ kg^{-1} and Si content > 43 mg kg^{-1}. Furthermore, 2 out of 9 combination rates (i. 2 t ha^{-1} calcium silicate + 2 t ha^{-1} GML, and ii. 3 t ha^{-1} calcium silicate + 2 t ha^{-1} GML) cost were below the cost of 4 t ha^{-1} GML value of USD 668, which is a common rate used by the farmers in Malaysia. Thus, possible recommendation are, i) 2 t ha^{-1} calcium silicate + 2 t ha^{-1} GML cost USD 484 and, ii) 3 t ha^{-1} calcium silicate + 2 t ha^{-1} GML cost USD 559. These combination rates met the desired requirement of soil chemical characteristics and could reduce the liming cost of rice-farmers in Malaysia under acid sulfate soil.

Keywords: acid sulfate soil; calcium silicate; ground magnesium limestone; submergence soil; soil amendments

INTRODUCTION

Department of Agriculture Malaysia, Ministry of Agriculture (2006) application of 1.5-5 t ha^{-1} based on soil acidity. Higher acidity soil requires more GML to neutralise the soil acidity and vice versa. The price of GML keeps increasing. For example, the price in 2010 and 2016 are USD 50 t ha^{-1} and USD 122 t ha^{-1}, respectively. Soratto & Crusciol (2008) stated that lime is not very soluble materials, and its dissociated components showed limited mobility. Considering those possible drawbacks (cost and mobility limitation) of GML, we also expect that the combination of GML with calcium silicate may improve the soil chemical characteristics and thus improve their soil ameliorative combined effects.

Besides, calcium silicate solubility is 6.78 times more soluble than lime (Alcarde & Rodella, 2003). Moreover, advantages of silicate compared to lime alone, are higher reaction rate and mobility down to deeper soil layers. Besides that, silicate in the form of silicon can strengthen crops against biotic and abiotic stresses on crops (Abed-Ashtiani et al., 2012; Hodson & Evans, 1995; Liang et al., 2007; Menzies et al., 2019; Peaslee & Frink, 1969; Romero-Aranda et al., 2006). Elisa et al. (2016) also reported that calcium silicate alleviates Al toxicity on acid sulfate soils of rice-cropped soil. Several authors have postulated their mechanism (Alcarde & Rodella, 2003; Nolla et al., 2013), as shown below:

$CaSiO_3 \rightarrow Ca^{2+} + SiO_3^{2-}$

$SiO_3^{2-} + H_2O_{\ (soil)} \rightarrow HSiO_3^{-} + OH^{-}$

$HSiO_3^{-} + H_2O_{\ (soil)} \rightarrow H_2SiO_3 + OH^{-}$

$H_2SiO_3 + H_2O_{\ (soil)} \rightarrow H_4SiO_4$

One way to reduce the acidity is by reducing the capability of H^+ to fill-in the soil exchange sites. With the addition of Ca source (calcium silicate) as soil amendments, the competition for exchange sites increase between Ca^{2+} and H^+, and often the exchange sites are occupied by Ca^{2+}. Meanwhile, the H^+ in the soil system can be bind by SiO_3^{2-} and becomes $HSiO_3^-$ (hydrogen silicate ion). A gradual release of Ca^{2+} and SiO_3^{2-} from calcium silicate, will continuously fill the exchange sites and reduce the potential of extra (free) H^+ availability in the soil system. With that, soil acidity can be reduced.

From the equations, silicate (SiO_3^{2-}) ions are released and subsequently, bind with the extra hydrogen (H^+) ion. Further reaction progress, as shown in the equation, leads to the formation of monosilicic acid (H_4SiO_4), which dissociates hydroxyl ions (OH^-). These hydroxyl ions can bind with Ca^{2+}, with continuous reaction, they will settle as Ca $(OH)_2$ in the soil system. When necessary, they can dissociate and supply Ca^{2+} to the soil. This will give continual liming effect to the acid sulfate soils, plus calcium is a macronutrient for the plant.

Moreover, also, these free hydroxyl ions may bind Al^{3+} to form inert Al-hydroxides (neutralise Al^{3+}) and bind with H^+ ions in the soil system and produce water molecules. Thus, with inert Al-hydroxides and minimal/less H^+ adsorbed to the exchangeable cations capacity, the soil pH increases (Lindsay, 1979); thus, soil acidity decreases. Those means that the combined effects of GML and calcium silicate may have additional benefits to alleviate soil acidity and improve crop resistance.

We examined the effect of the combination of GML and calcium silicate on the improvement of acid sulfate soils and showed that the proper level combination of the both showed distinct effects to achieve recommended values of selected soil chemical properties. Those values are:

i) Soil pH > 4 (Jusop Shamshuddin, 2006)

ii) Exchangeable Al < 2 $cmol_c\,kg^{-1}$ (Hiradate et al., 2007)

iii) Exchangeable Ca > 2 $cmol_c\,kg^{-1}$ (Palhares de Melo et al., 2001)

iv) Exchangeable Mg > 1 $cmol_c\,kg^{-1}$ (Dobermann & Fairhurst, 2000)

v) Si content > 43 mg kg^{-1} (Narayanaswamy & Prakash, 2009)

This paper aimed to evaluate the efficiency of calcium silicate with and/or without GML application on soil chemical characteristics and to find the optimal recommendation rate considering the positive effect of soil chemical characteristics and the costs incurs.

MATERIALS AND METHODS

Soil Used in the Study

Acid sulfate soils were used in this study classified as Typic Sulfaquepts, was collected from Merbok, Kedah, Peninsular Malaysia. The soil sampling site was a rice-cropped area, and the sampling was performed one month before rice cultivation (dry condition). A composite soil sample of approximately 100 kg was taken from topsoil (0-15 cm) depth using an auger for submergence experiment. The sample was taken within a 0.5 ha region of the rice-cropped area. Samples for soil characterisation were taken with a soil auger at five different depths (Table I). The samples were placed in plastic bags and transported back immediately to the Laboratory, Universiti Putra Malaysia for soil chemical characteristic analyses.

Soil Treatments and Experimental Design

The submergence experiment was conducted at Ladang 2, Universiti Putra Malaysia under rain shelter condition. Two types of soil amendments were used; i) ground magnesium limestone (GML) (0, 2, 4 and 6 t ha^{-1}) and ii) calcium silicate (0, 1, 2 and 3 t ha^{-1}) was arranged in a completely randomised design (CRD) with three replications. The GML used in this experiment was obtained from Britestone Sdn. Bhd., Malaysia. It is made of Dolomitic Limestone milled to a very fine powder with the criteria of 100% passing thru a 20-mesh screen, 70% passing thru a 100-mesh screen and more than 40% passing thru a 200-mesh screen. The chemical content of

GML were CaO = 31-38%, MgO = 15-18%, SiO_2 < 0.2% and Fe_2O_3 < 0.1%. The calcium silicate ($CaSiO_3$) used in this experiment was obtained from Kaolin (Malaysia) Sdn. Bhd., Malaysia. This calcium silicate (as CaO) = 40-50, Al_2O_3 = below 1.5, MgO = below 3, iron (as Fe_2O_3) = below 1% and pH = 8.54.

Five hundred grams of air-dried acid sulfate soils passed through 2 mm sieve was placed in a plastic pot. The soil samples were mixed with soil amendments and inundated with water. The water level was maintained 5 cm from the soil surface throughout the experiment. The pH of the water used was 7.37. The composition of water in relation to phosphorus (P), potassium (K), aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), and silicon (Si) was 0.74, 10.62, 0.14, 19.78, 0.03, 1.00 and 5.18 mg L^{-1}, respectively (Elisa et al., 2016).

Soil and Water Analyses

Soil and water sampling were carried out four times during the experiment at (i) 30 days (30D); (ii) 60 days (60D); (iii) 90 days (90D); and (iv) 120 days (120D) correspond to typical rice growth stages; vegetative, reproductive, flowering and maturity stages, respectively. The collected soil samples were air-dried, ground and passed through a 10-mesh sieve (2 mm) for soil analyses. The following soil analyses were carried out to the collected samples: (i) Soil pH was determined in 1: 2.5 (soil to water ratio) using pH meter (PHM 93 Radiometer), (ii) determination of exchangeable Al was determined by extracting 5 g soil with 50 mL of 1 M KCL. The mixture was shaken for 30 min and analysed by ICP-OES (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA)., (iii) extractable Fe, Cu, Zn and Mn were extracted using Double Dilute Acid method; with 0.05 M HCl in 0.0125 M H_2SO_4 in 1:5 ratios. Five (5) g of air-dried soil was mixed with 25 mL of extracting agent and shaken for 15 minutes at 180 rpm. The supernatant was then filtered using filter paper Whatman No. 42 and determined using Atomic Absorption Spectrometry (AAS Perkin Elmer, model 1100B); (iv) exchangeable K, Ca, Mg, Na and Fe were extracted using 1 N NH_4Cl (Jusop Shamshuddin, 2006). Briefly, 2 g of air-dried soil was put in a 50 mL centrifuge tubes and added 20 mL 1 M NH_4Cl. After intermittent shaking for 2 hours, the tubes were centrifuged at 2500 rpm for 15 minutes. The supernatant was transferred and filtered using filter paper Whatman No. 42. The exchangeable K, Ca, Mg, Na and Fe in the extract were determined by ICP-OES (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA); (v) Cation exchange capacity (CEC) of the soil was determined using 1M NH_4OA_c at pH7 (Chapman, 2016); (vi) meanwhile, Si was extracted using 0.01 M $CaCl_2$ proposed by Narayanaswamy & Prakash, (2009). Two (2) g of air-dried soil was shaken for 16 hours with 20 mL extractant in a 50 mL Nalgene tube using an end-over-end shaker. After centrifuging at 2000 rpm for 10 minutes, the supernatant was analysed for Si using ICP-OES (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA) and (vii) Total C, N and S were determined using CNS Analyzer (Leco RC-412C Leco Corporation, St. Joseph MI).

Collected water samples were filtered using filter paper Whatman No.42. Water pH was determined using a pH meter (PHM 93 Radiometer). The concentration of Al was determined using ICP-OES (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA).

Statistical Analysis

Data from the experiment were analysed statistically using analysis of variance (ANOVA) and response surface curve, correlation, polynomial regression and multiple comparisons (Tukey's test) were employed using a statistical package, SAS v 9.1.

RESULTS

Soil pH Changes

Initial soil pH was pH 2.89. Soil pH increased with days of incubation, ranging from pH 3.62-4.53 for 30D, pH 3.63-4.55 for 60D, pH 3.40-4.52 for 90D, and pH 3.65-4.64 for 120D, as shown in Figure 1a-d. It was observed that the soil pH gradually increased with the increment in the rate of GML incorporated with calcium silicate. At 30D, the soil treated with 2, 4 and 6 t ha^{-1} of GML under each of 0, 1, 2 and 3 t ha^{-1} of calcium silicate significantly increased the soil pH compared to the soil pH without GML. At 60D, the soil that received 2 and 6 t ha^{-1} of GML significantly increased the soil pH under 0 and 1 t ha^{-1} of calcium silicate, respectively compared to the soil pH without GML. The soil pH at 90D slightly decreased under all the treated soil compared to the soil pH in 30D and 60D. In comparison to the soil without GML, 6 t ha^{-1} GML significantly increased the soil pH with the combination of 0, 2 and 3 t ha^{-1} of calcium silicate. Further increases in soil pH were observed at 120D. The soil with 2 t ha^{-1} GML significantly increased the soil pH compared to the soil without GML under 0 t ha^{-1} calcium silicate.

Exchangeable Al and Al Saturation Changes

Initially, the exchangeable Al and Al saturation were 5.18 $cmol_c$ kg^{-1} and 49.95%, respectively. The exchangeable Al (Figure 1e-h) and Al saturation (Figure 1i-l) were reduced after the addition of the soil amendments corresponding with the incubation period. Under 0, 2 and 3 t ha^{-1} of calcium silicate, the soil treated with 2, 4, and 6 t ha^{-1} of GML significantly decreased the exchangeable Al compared to the soil without GML at 30D. On the other hand, the soil under 1 t ha^{-1} calcium silicate significantly decreased the exchangeable Al in-combination with 4 and 6 t ha^{-1} GML compared to 0 and 2 t ha^{-1} GML. In comparison to the soil without GML, the soil with

2, 4, and 6 t ha^{-1} were significantly decreased the exchangeable Al under 0, 1 and 2 t ha^{-1} of calcium silicate at 60D. The exchangeable Al values in the soil without GML were significantly higher compared to the other GML treatments at 90D. Meanwhile, at 120D, the exchangeable Al significantly reduced for 2, 4 and 6 t ha^{-1} of GML compared to the soil without GML under each of calcium silicate treatments (0, 1, 2 and 3 t ha^{-1}). When compared to soil without GML, the soil treated with 2, 4 and 6 t ha^{-1} of GML significantly reduced the Al saturation with the combination of each calcium silicate application for the entire incubation period. The Al saturation was 49.95% before the incubation and below 35% at 30D. The Al saturation in soil without GML were significantly higher compared to other GML treatments at 30D, 60D, 90D and 120D. The most significant differences in the Al saturation occurred during the first 30 days, and the rate of decrease was the higher with, the higher the GML content. At 120D, the Al saturation was at its lowest (nearly 0%).

Exchangeable Ca and Mg Changes

The soil treated with calcium silicate and GML recorded an increase of exchangeable Ca and Mg in the soil. Figure 1m-p shows the increase of the exchangeable Ca by GML and calcium silicate addition for the entire incubation period. Compared to the soils without GML, significant increases in exchangeable Ca were observed under the GML treatments with the different rate (0, 1, 2, 3 t ha^{-1}) of calcium silicate addition at 30D, 60D and 120D, respectively. On the other hand, the exchangeable Mg (Figure 1q-t) significantly increased with the soil treated with GML (2, 4, 6 t ha^{-1}) under the different rates of calcium silicate compared to GML at 30D and 60D.

Si Content Changes

The initial Si value was 25.8 mg kg^{-1} in the soils. Table II shows the Si value ranges of each incubation day summarised based on Figure 1u-x. The increment of the Si values was marked with the increase in the days of incubation. A sigmoid (s-curve) increment trend was noted. In both reproductive and flowering stages, the Si content ranges were higher than 43 mg kg^{-1} under any combinations of the soil amendments while a combination level (3 t ha^{-1} calcium silicate) achieved the value in the vegetative stage. The result indicates that the soil amendment (calcium silicate) has the potential to release sufficient Si to the soil for plant uptake at least at the 60^{th} day. The released Si is expecting to be in the available form, and this form complements well with the crop requirements.

DISCUSSION

Soil Acidity Reduction With Time

Figure 2 shows the relationship between soil pH and exchangeable Al for the entire incubation periods. Exchangeable Al negatively correlated with the soil pH. Exchangeable Al decrease as the soil pH increased. It shows that the lines at 60D, 90D and 120D were shifted to the left. The line shift to the left indicates that Al toxicity decreased as the incubation period increased. The line shift at 90D was below 120D, and this is believed to take place due to the release of protons as pyrite in the soil was oxidised during the incubation period. The oxidation of pyrite, which produces acidity, may have taken place according to the following reactions outlined by (Breemen, 1976):

$$2\ FeS_{2(s)} + 7\ O_{2\ (aq)} + 2\ H_2O \rightarrow Fe^{2+}_{(aq)} + 4\ SO_4^{2-} + 4\ H^+_{(aq)} \qquad (1)$$

Further oxidation of Fe^{2+} to Fe^{3+} oxide could also promote acidity:

$$2\ Fe^{2+}_{(aq)} + \frac{1}{2}\ O_{2\ (aq,g)} + H_2O \rightarrow Fe_2O_{3(s)} + 4H^+_{(aq)} \qquad (2)$$

The results from the current study are consistent with those from other studies of acid sulfate soils (Shamshuddin et al., 1995, 2014; Jusop Shamshuddin & Auxtero, 1991). It is shown in Eqs. (1) and (2) that one mole of pyrite produces four moles of sulfuric acid. This free acidity is partly responsible for the dissolution of clay minerals, resulting in the release of metals like Al into the soils, shown by Figure 1h. Furthermore, Shamshuddin et al. (2004) reported that soil pH in the Cg horizon (subsoil) was lowered by 1 unit after 12 weeks of incubation.

The soil pH (Figure 2) did not exceed pH 5 compared to the water solution pH, as shown in Figure 3. At 30D (Figure 3a), Al_{water} concentration decreased with the increment in the water solution pH. The Al_{water} concentration was observed to gradually increase at 60D (Figure 3b), 90D (Figure 3c) and 120D (Figure 3d). Their gradual improvement will support positive crop growth inline with vegetative, reproductive, flowering and maturity paddy stages.

GML and Calcium Silicate Combined Ameliorative Effects on the Selected Soil Characteristics

In this section, we first discuss the chemical mechanism of soil amendments used in this study regarding their effects in alleviating soil acidity and improving soil fertility. Second, we will present the advantages of applying combination soil amendments instead of a single application of GML or calcium silicate in achieving better soil chemical characteristics at the 30th days of incubation. Finally, we try to find out the most optimal combination of the application levels of both calcium silicate and GML as a recommendation rate to the farmers at the respective area in Malaysia. The recommendation rate will be evaluated based on the following factors;

i) The positive effect of chemical soil characteristics at the 30th days of incubation.

There are two reasons to focus on the data from the 30th days of the incubation. First, the acidity gradually decreases in soil (Figure 2) and water (Figure 3). This will support positive crop growth inline with vegetative, reproductive and flowering of rice growth phases. Second, it is more time-suitable for them otherwise they need to wait too long before they start planting and;

ii) Cost incurs for soil amendments application.

Because farmers are currently using GML at the rate of 4 t $ha^{-1,}$ which costs approximately USD 668, we seek for the optimal combinations of calcium silicate and GML to reduce the cost.

Calcium silicate was used to replace calcium silicate slag due to regulations in Malaysia, Environmental Quality Act 1974, that prohibits direct use of solid waste onto the soil for crop production and other means.

It is possible to postulate five different mechanisms of Al toxicity reduction by Si-rich compounds. Firstly, monosilicic acids can increase soil pH (Lindsay, 1979). Secondly, monosilicic acids can be adsorbed on aluminium hydroxides, impairing their mobility (Panov et al., 1982). Thirdly, soluble monosilicic acid can form slightly soluble substances with ions of Al (Lumsdon & Farmer, 1995). Another possibility for Al toxicity reduction by Si-rich compounds can be strong adsorption of mobile Al on silica surfaces (Schulthess & Tokunaga, 1996). Lastly, mobile silicon compounds can increase plant tolerance to Al (Rahman et al., 1998). All of these mechanisms may occur simultaneously, with certain ones prevailing under various soil conditions.

GML is well known to increase the soil pH, and release Ca and Mg into the soil system. GML ameliorative reactions are shown below:

$(Ca, Mg)(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ (equation 1)

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$ (equation 2)

$Al^{3+} + 3\ OH^- \rightarrow Al\ (OH)_3$ (equation 3)

GML dissolves gradually into the soil, and releases Ca and Mg (equation 1), and these macronutrients could be taken up by the growing rice plants. Subsequently, the hydrolysis of CO_3^{2-} (equation 2) would produce hydroxyls that neutralise Al by forming inert Al-hydroxides (equation 3). Combination of calcium silicate and GML, both shows the significant ameliorative effect with; i) release of Ca, ii) binding of Al^{3+} making it inert Al-hydroxides and, iii) bind H^+ to produce water molecules.

Figure 4a shows that exchangeable Al decreased with increment in soil pH. The addition of calcium silicate alone could reduce the exchangeable Al below the critical value (< 2 $cmol_c\ kg^{-1}$) and soil pH higher than 4 to avoid their inhibitory effects on rice growth. The distribution pattern shifted to the right when the soil was treated with both GML and calcium silicate, indicating the combined ameliorative effects of both soil amendments. Under most of the combinations of both amendments with different application levels, the exchangeable Al and soil pH values fall within the critical values (Al < 2 $cmol_c\ kg^{-1}$ and soil pH > 4). Thus, the result indicates that the addition of both soil amendments improved the acid sulfate soils compared to single soil amendment application.

Figure 4b shows silicon content was negatively correlated with exchangeable Al under application of calcium silicate only, keeping the Al level higher than the critical value of 2 $cmol_c$

kg^{-1}. The Si content was lower than sufficient level (> 43 mg kg^{-1}) for crop growth only with GML though the exchangeable Al is lower than the critical value. Direct correlation of Si in soil solution with Al phytotoxicity in soil solution was recorded by (Cocker et al., 1998); Si content increase while Al decrease. These results suggest that the interaction between aluminium and silicon occur in solution, probably by the formation of a complex between aluminium and silicon that is not toxic to plants. Studies conducted by Elisa et al. (2016) and Myhr & Erstad (1996) showed that Si could effectively reduce Al toxicity. Under a proper combination of application levels of the both of the amendments, exchangeable Al were lower than 2 $cmol_c$ kg^{-1}, while Si contents > 43 mg kg^{-1}compared to the application of GML or calcium silicate only.

Figure 4c shows soil pH positively correlates with silicon content under the calcium silicate application alone. The application of one type of soil amendments alone, either calcium silicate or GML, was unable to increase the soil pH above 4 and the silicon content above 43 mg kg^{-1}, respectively. Statistically, no significant relationships between soil pH and silicon content were observed for soil treated with the only GML and with the combination of both soil amendments. However, the distribution pattern shifted to the right in the soil with GML and the combination of calcium silicate and GML. Some of the combined applications were able to fulfil above the recommended levels.

Figure 4d shows that exchangeable Ca negatively correlates with exchangeable Al. As the exchangeable Ca increased, the exchangeable Al decreased. Single or combined application of soil amendments made the exchangeable Ca reach the requirement of 2 $cmol_c$ kg^{-1}. However, the application of calcium silicate alone did not reduce the exchangeable Al below the critical level of 2 $cmol_c$ kg^{-1} while the exchangeable Al was reduced below the critical level for application of GML alone and the combination.

Figure 4e shows that exchangeable Mg increased as the exchangeable Al decreased. The addition of calcium silicate alone did not decrease the exchangeable Al below the critical level of 2 $cmol_c$ kg^{-1}. On the other hand, the addition of GML alone or the combination of both soil amendments decreased the exchangeable Al below the critical level of 2 $cmol_c$ kg^{-1}. The application of the soil amendments alone or with the combination increased in exchangeable Mg above the required level of 1 $cmol_c$ kg^{-1}.

Effective Combination Rate of Calcium Silicate and GML as Soil Amendments

The combination rate in yellow colour achieved the recommended level for soil pH (Table IIIa), exchangeable Al (Table IIIb), exchangeable Ca (Table IIIc), exchangeable Mg (Table IIId) and Si content (Table IIIe) of > 4 (Jusop Shamshuddin, 2006), < 2 $cmol_c$ kg^{-1} (Hiradate et al., 2007), > 2 $cmol_c$ kg^{-1} (Palhares de Melo et al., 2001), > 1 $cmol_c$ kg^{-1} (Dobermann & Fairhurst, 2000) and > 43 mg kg^{-1} (Narayanaswamy & Prakash, 2009), respectively.

Finally, Table IV shows the soil chemical characteristics which meet the recommended level for each combination of calcium silicate and GML. It shows that a combination of 3 t ha^{-1} calcium silicate with 2, 4 or 6 t ha^{-1} GML achieved the recommended levels for all the five soil chemical characteristics of, the soil pH, exchangeable Al, Ca, Mg and Si content (marked in green colour). The combination of 2 t ha^{-1} calcium silicate with 2 t ha^{-1} of GML achieved the recommended levels of 4 soil chemical characteristics out of 5 (marked in yellow colour), the exchangeable Al, Ca, Mg and Si content. Though the recommended soil pH of 4 was not achieved in this combination, the value, pH 3.98 was very close to 4. The combined rate of GML, 2 t ha^{-1} calcium silicate with 4 t ha^{-1} GML, 2 t ha^{-1} calcium silicate with 6 t ha^{-1} GML, 1 t ha^{-1} calcium silicate with 4 t ha^{-1} GML and 2 t ha^{-1} calcium silicate with 6 t ha^{-1} GML achieved the recommended levels of 4 soil chemical characteristics out of 5 (marked in yellow color), the soil pH, exchangeable Al, Ca and Mg. In those combinations, Si was below the recommended value of 43 mg kg^{-1}. The remaining combination rate of calcium silicate and GML achieved 3 or less of the recommended level for soil chemical characteristics.

In this study, we will consider, the combination of calcium silicate and GML, which achieved 4 and 5 of recommended levels. Those combination rates will be further analysed for the feasibility analysis to find out the most optimal combination balancing the fertility improvement and the cost-effectiveness.

Feasibility Analysis

Table V shows the cost incurs for soil amendments application. The cost includes the price of soil amendments and labour cost. Currently, the price for both calcium silicate slag and GML is USD 30 t^{-1} and USD 122 t^{-1}, respectively, while the labour cost incurs at USD 45 t^{-1}. Currently, farmers at the respective area use 4 t of GML ha^{-1} with the cost of USD 668 (marked in green colour). Therefore, the total cost of less than USD 668 was considered. From Table IV, it shows that 9 out of 16 combinations achieved 4 or 5 of the recommended level for soil chemical characteristics. However the costs for the combination of 2 t ha^{-1} calcium silicate with 2 t ha^{-1} GML and 3 t ha^{-1} calcium silicate with 2 t ha^{-1} GML were less from USD 668; USD 484 and USD 559, respectively (Table V) (marked in yellow colour).

Out of the possible two recommendations, the combination of 3 t ha^{-1} calcium silicate with 2 t ha^{-1} GML achieved the recommended levels of all the targeted soil characteristics. The costs differences between the combination and the common practice with 4 t ha^{-1} of GML are USD 154 (USD 488 - USD 334) for only the soil amendment cost and USD 109 (USD 668 -

USD 559) for the total cost including labor cost, meaning that this recommendation is USD 114 more beneficial per ha (16% less) for the farmers.

Another possible recommendation of 2 t ha^{-1} calcium silicate with 2 t ha^{-1} GML did not achieve the pH 4 but the recommended levels of the exchangeable Al, Ca, Mg and Si content. The pH level of the combination was, however, pH 3.98, which was very close to the recommended level of 4. In this combination, the costs differences between the combination and the common practice with 4 t ha^{-1} of GML are USD 184 (USD 488 - USD 304) for only the soil amendment cost and USD 184 (USD 668 - USD 484) for the total cost including labor cost, meaning that this recommendation is USD 184 more beneficial per ha (28%) for the farmers. In this study, the pH level under the standard practice with 4 t ha^{-1} of GML was also 3.98 (Table III a) which is below the recommended level and the same as that of this recommendation. Moreover, under the condition of the common practice, Si did not achieve the recommended level of 43 mg kg^{-1} (Table III e), indicating that the combination of 2 t ha^{-1} calcium silicate with 2 t ha^{-1} GML may improve rice growth better than the standard practice in addition to the cost reduction of USD 184. Therefore, the combination can be advantageous for the farmers despite the pH level.

Both of the recommendations are more beneficial than conventional practice. In term of the total cost, the combination of 2 t ha^{-1} calcium silicate with 2 t ha^{-1} GML is better than the combination of 3 t ha^{-1} calcium silicate with 2 t ha^{-1} GML, though the pH level is below 4 for the former case. If farmers can expect that improvement of the yield under the later combination compensates the cost difference between two recommendations, the choice can be the latter. At this moment, we do not have the information about the relationship between the combination and the yield, and we need further studies to conclude the recommendation, considering the expected yield. With such information, other combinations which achieved the recommended levels of 5 soil characteristics (3 t ha^{-1} calcium silicate with 4 t ha^{-1} GML and 3 t ha^{-1} calcium silicate with 6 t ha^{-1} GML) can be under consideration as higher yield may be able to compensate the cost increase

CONCLUSION

The possible recommendation rate is 2 t ha^{-1} calcium silicate with 2 t ha^{-1} GML price at USD 484 and 3 t ha^{-1} calcium silicate with 2 t ha^{-1} GML price at USD 559. That recommendation rate achieved the recommended levels of soil pH, exchangeable Al, Ca, Mg and Si content with the total cost below than common practice now at Malaysia value of USD 668.

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REFERENCES

Abed-Ashtiani, F., Kadir, J.-B., Selamat, A.-B., Husni, A., Hanif, B.-M., & Nasehi, A. (2012). Effect of Foliar and Root Application of Silicon Against Rice Blast Fungus in MR219 Rice Variety. *Plant Pathol. J*, *28*(2), 164–171. https://doi.org/10.5423/PPJ.OA.02.2012.0022

Alcarde, J., & Rodella, A. (2003). Quality and legislations of fertilizer and acidity correction sourcesNo Title. In N. Curi, J. Marques, L. Guilherme, J. Lima, A. Lopes, & V. Alvares (Eds.), *Topics in Soil Science* (pp. 291–334).

Breemen, N. van. (1976). *Genesis and solution chemistry of acid sulfate soils in Thailand*.

https://library.wur.nl/WebQuery/wurpubs/70246

Chapman, H. D. (2016). Cation-Exchange Capacity. In *Agronomy Journal* (Vol. 9, pp. 891–901). John Wiley & Sons, Ltd. https://doi.org/10.2134/agronmonogr9.2.c6

Cocker, K. M., Evans, D. E., & Hodson, M. J. (1998). The amelioration of aluminium toxicity by silicon in higher plants: Solution chemistry or an in planta mechanism? *Physiologia Plantarum*, *104*(4), 608–614. https://doi.org/10.1034/j.1399-3054.1998.1040413.x

Department of Agriculture Malaysia, Ministry of Agriculture, M. (2006). *Manual tanaman padi (Rice planting handbooks, manual)*. Perpustakaan Negara Malaysia.

Dobermann, A., & Fairhurst, T. (2000). *Nutrient Disorders & Nutrient Management Rice Rice ecosystems Nutrient management Nutrient deficiencies Mineral toxicities Tools and information*.

Elisa, A. A., Ninomiya, S., Shamshuddin, J., & Roslan, I. (2016). Alleviating aluminum toxicity in an acid sulfate soil from Peninsular Malaysia by calcium silicate application. *Solid Earth*, *7*(2), 367–374. https://doi.org/10.5194/se-7-367-2016

Hiradate, S., Ma, J. F., & Matsumoto, H. (2007). Strategies of Plants to Adapt to Mineral Stresses in Problem Soils. In *Advances in Agronomy* (Vol. 96, pp. 65–132). Academic Press. https://doi.org/10.1016/S0065-2113(07)96004-6

Hodson, M. J., & Evans, D. E. (1995). Aluminium/silicon interactions in higher plants. In *Journal of Experimental Botany* (Vol. 46, Issue 2, pp. 161–171). Oxford Academic. https://doi.org/10.1093/jxb/46.2.161

Liang, Y., Sun, W., Zhu, Y. G., & Christie, P. (2007). Mechanisms of silicon-mediated alleviation of abiotic stresses in higher plants: A review. *Environmental Pollution*, *147*(2), 422–428. https://doi.org/10.1016/j.envpol.2006.06.008

Lindsay, W. . (Ed.). (1979). *Chemical equilibria in soils* . https://www.worldcat.org/title/chemical-equilibria-in-soils/oclc/681210219

Lumsdon, D. G., & Farmer, V. C. (1995). Solubility characteristics of proto-imogolite sols: how silicic acid can de-toxify aluminium solutions. *European Journal of Soil Science*, *46*(2), 179–186. https://doi.org/10.1111/j.1365-2389.1995.tb01825.x

Menzies, J., Bowen, P., Ehret, D., & Glass, A. D. M. (2019). Foliar Applications of Potassium Silicate Reduce Severity of Powdery Mildew on Cucumber, Muskmelon, and Zucchini Squash. *Journal of the American Society for Horticultural Science*, *117*(6), 902–905. https://doi.org/10.21273/jashs.117.6.902

Myhr, K., & Erstad, K. (1996). Converter slag as a liming material on organic soils. *Norwegian J. Agric. Sci.*, *10*(1), 83–93. https://agris.fao.org/agris-search/search.do?recordID=NO9600123

Narayanaswamy, C., & Prakash, N. B. (2009). Calibration and categorization of plant available silicon in rice soils of South India. *Journal of Plant Nutrition*, *32*(8), 1237–1254. https://doi.org/10.1080/01904160903005970

Nolla, A., Henrique Korndörfer, G., Amaral Tavares Da Silva, C., Roque Benetoli Da Silva, T., Zucarelli, V., & Anita Gonçalves Da Silva, M. (2013). *Correcting soil acidity with the use of slags*. *8*(41), 5174–5180. https://doi.org/10.5897/AJAR2013.6940

Palhares de Melo, L. A. M., Bertioli, D. J., Cajueiro, E. V. M., & Bastos, R. C. (2001). Recommendation for fertilizer application for soils via qualitative reasoning. *Agricultural Systems*, *67*(1), 21–30. https://doi.org/10.1016/S0308-521X(00)00044-5

Panov, N., Goncharova, N., & Rodionova, L. (1982). The role of amorphous silicic acid in solonetz soil processes. *Vestnik Agr. Sci.*, *11*, 18.

Peaslee, D. E., & Frink, C. R. (1969). Influence of Silicie Acid on Uptake of Mn, Al, Zn, and Cu by Tomatoes (Lycopersicum esculentum) Grown on an Acid Soil. *Soil Science Society of America Journal*, *33*(4), 569–571. https://doi.org/10.2136/sssaj1969.03615995003300040025x

Rahman, M. T., Kawamura, K., Koyama, H., & Hara, T. (1998). Varietal differences in the growth of rice plants in response to aluminum and silicon. *Soil Science and Plant Nutrition*, *44*(3), 423–431. https://doi.org/10.1080/00380768.1998.10414464

Romero-Aranda, M. R., Jurado, O., & Cuartero, J. (2006). Silicon alleviates the deleterious salt effect on tomato plant growth by improving plant water status. *Journal of Plant Physiology*, *163*(8), 847–855. https://doi.org/10.1016/j.jplph.2005.05.010

Schulthess, C. P., & Tokunaga, S. (1996). Metal and pH Effects on Adsorption of Poly(vinyl alcohol) by Silicon Oxide. *Soil Science Society of America Journal*, *60*(1), 92–98. https://doi.org/10.2136/sssaj1996.03615995006000010016x

Shamshuddin, J., Elisa Azura, A., Shazana, M. A. R. S., Fauziah, C. I., Panhwar, Q. A., & Naher, U. A. (2014). Properties and management of acid sulfate soils in Southeast Asia for sustainable cultivation of rice, oil palm, and cocoa. In *Advances in Agronomy* (Vol. 124). https://doi.org/10.1016/B978-0-12-800138-7.00003-6

Shamshuddin, J., Jamilah, I., & Ogunwale, J. A. (1995). Formation of hydroxy-sulfates from pyrite in coastal acid sulfate soil environments in malaysia. *Communications in Soil Science and Plant Analysis*, *26*(17–18), 2769–2782. https://doi.org/10.1080/00103629509369486

Shamshuddin, J., Muhrizal, S., Fauziah, I., & Van Ranst, E. (2004). A Laboratory Study of Pyrite Oxidation in Acid Sulfate Soils. *Communications in Soil Science and Plant Analysis*, *35*(1–2), 117–129. https://doi.org/10.1081/CSS-120027638

Shamshuddin, Jusop. (2006). *Acid Sulfate Soils in Malaysia*. Universiti Putra Malaysia Press.

Shamshuddin, Jusop, & Auxtero, E. (1991). Soil solution compositions and minerology of some active aci sulfate soils in Malaysia as affected by laboratory incubation with lime. *Soil Science*, *152*(5). https://journals.lww.com/soilsci/Fulltext/1991/11000/SOIL_SOLUTION_COMPOSITIONS_AND_MINERALOGY_OF_SOME.8.aspx

Soratto, R. P., & Crusciol, C. A. C. (2008). Dolomite and Phosphogypsum Surface Application Effects on Annual Crops Nutrition and Yield. *Agronomy Journal*, *100*(2), 261–270. https://doi.org/10.2134/agronj2007.0120

Table I. Initial soil chemical characteristics of soils from Merbuk (Kedah)

Depth (cm)	Soil soil: water 1:2.5	Exchangeable cation K	Ca	Mg	Na	Al	CEC	ECEC	Extractable Fe	Cu	Zn	Mn	Si	Total C	N	S	Al saturatio %
		---------------------cmol$_c$ kg^{-1}---------------------							----------------mg kg^{-1}----------------					---------%---------			
0-15	2.89	0.44	0.85	2.01	1.89	5.18	16.02	10.37	624.80	1.00	3.75	2.90	25.80	2.34	0.14	0.10	49.95
15-30	2.93	0.44	0.80	1.92	1.97	5.26	15.55	10.39	500.50	0.95	3.50	2.80	24.40	2.24	0.11	0.10	50.62
30-45	2.82	0.48	0.89	2.21	2.36	5.20	14.59	11.14	396.80	0.80	3.35	2.90	21.50	2.41	0.10	0.16	46.67
45-60	2.22	0.35	0.94	2.61	2.40	6.18	16.54	12.48	435.10	1.00	3.85	3.35	24.40	3.18	0.10	0.60	49.51
60-75	2.32	0.63	2.74	9.71	4.67	6.66	17.18	24.41	584.40	1.10	6.95	6.05	38.40	3.49	0.11	1.54	27.28

Table II. Summary of the Si values (ranges and means) of each incubation days. Means marked with the same letter are not significantly different at p < 0.05 (Tukey's Test)

Stage	Days of incubation (D)	Si (mg kg^{-1})	Means value
1 month after soil amendments application	30D	23.80-50.12	37.19^{c}
Vegetative stage	60D	16.46-40.81	29.00^{d}
Reproductive stage	90D	55.35-96.86	70.78^{b}
Flowering stage	120D	52.06-96.33	81.01^{a}

Table III. Effect of calcium silicate in-combination with GML on soil pH (a), exchangeable Al (b), exchangeable Ca (c), exchangeable Mg (d) and Si content (e) at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at *p* < 0.05 (Tukey`s Test) (The combination rate in yellow colour achieved the recommended level of each chemical soil characteristic)

a

	Calcium silicate (t ha^{-1})			
GML (t ha^{-1})	0	1	2	3
0	3.63^{b}	3.62^{d}	3.77^{d}	3.75^{d}
2	3.97^{a}	3.88^{c}	3.98^{c}	4.03^{c}
4	3.98^{a}	4.09^{b}	4.18^{b}	4.30^{b}
6	4.26^{a}	4.34^{a}	4.40^{a}	4.53^{a}

b

	Calcium silicate (t ha^{-1})			
GML (t ha^{-1})	0	1	2	3
0	3.34^{a}	2.91^{a}	2.36^{a}	2.14^{a}
2	1.92^{b}	1.58^{a}	1.44^{b}	1.20^{b}
4	1.64^{b}	1.17^{b}	0.82^{c}	0.63^{c}

c

	Calcium silicate (t ha^{-1})			
GML (t ha^{-1})	0	1	2	3
0	2.41^{c}	3.06^{d}	3.75^{d}	4.19^{c}
2	3.73^{b}	4.05^{c}	4.53^{c}	5.26^{b}
4	4.13^{b}	4.72^{b}	5.51^{b}	6.44^{a}
6	5.08^{a}	5.78^{a}	6.12^{a}	6.90^{a}

d

GML (t ha^{-1})	Calcium silicate (t ha^{-1}) 0	1	2	3
0	3.13^{c}	2.99^{c}	3.15^{c}	3.41^{c}
2	3.79^{b}	4.15^{b}	4.09^{b}	4.13^{b}
4	4.16^{b}	4.59^{b}	4.57^{ab}	5.03^{a}
6	4.84^{a}	5.22^{a}	4.94^{a}	5.21^{a}

e

GML (t ha^{-1})	Calcium silicate (t ha^{-1}) 0	1	2	3
0	30.65^{a}	29.90^{b}	40.84^{a}	44.82^{ab}
2	29.48^{ab}	33.02^{ab}	43.80^{a}	51.79^{a}
4	23.80^{b}	33.73^{ab}	38.09^{a}	50.12^{ab}
6	26.50^{ab}	37.13^{a}	38.08^{a}	43.21^{b}

Table IV. Combination of calcium silicate with GML achieves the recommended value of soil chemical characteristics. (Combination rate achieved 4 out of 5 recommended level

marked with yellow while the combination rate achieved five recommended level marked with green)

	Calcium silicate (t ha^{-1})			
GML (t ha^{-1})	0	1	2	3
0	Ca Mg	Ca Mg	Ca Mg Si	Ca Mg Si
2	Al Ca Mg	Al Ca Mg	**Al** **Ca** **Mg** **Si**	**pH** **Al** **Ca** **Mg** **Si**
4	Al Ca Mg	**pH** **Al** **Ca** **Mg**	**pH** **Al** **Ca** **Mg**	**pH** **Al** **Ca** **Mg** **Si**
6	**pH** **Al** **Ca** **Mg**	**pH** **Al** **Ca** **Mg**	**pH** **Al** **Ca** **Mg**	**pH** **Al** **Ca** **Mg** **Si**

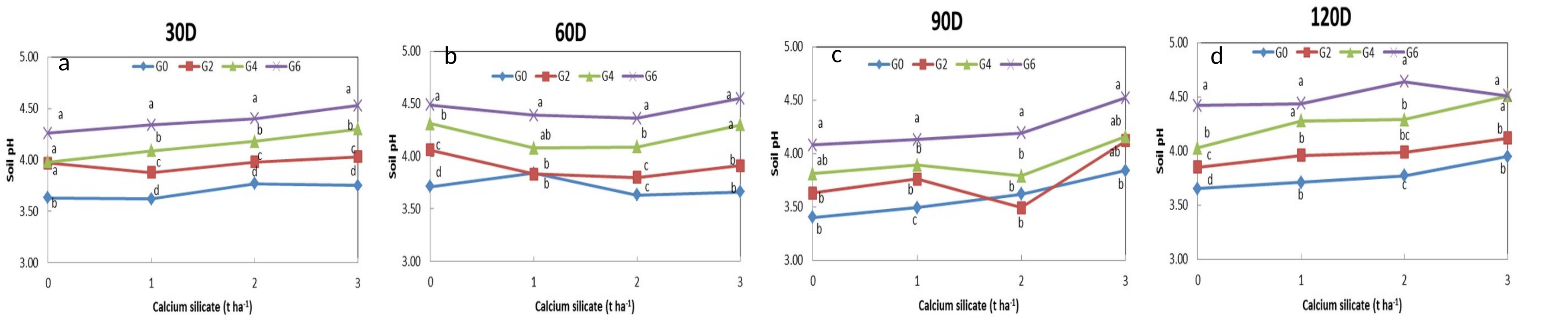
Table V. Cost incurs for application of soil amendments (Green indicate the common practice while yellow indicate total cost below the common practice and achieved 4 or 5 recommended level of soil chemical characteristics.

	Calcium silicate (t ha^{-1})			
GML (t ha^{-1})	0	1	2	3
0	SA: 0 L: 0 T: 0	SA: 30 L: 45 T: 75	SA: 60 L: 90 T: 150	SA: 90 L: 135 T: 225
2	SA: 244 L: 90 T: 334	SA: 274 L: 135 T: 409	**SA: 304 L: 180 T:484**	**SA: 334 L: 225 T: 559**
4	SA: 488 L: 180 T: 668	SA: 518 L: 225 T: 743	SA: 548 L: 270 T: 818	SA: 578 L: 315 T: 893
6	SA: 732 L: 270 T: 1002	SA: 762 L: 315 T: 1077	SA: 792 L: 360 T: 1152	SA: 822 L: 405 T: 1227

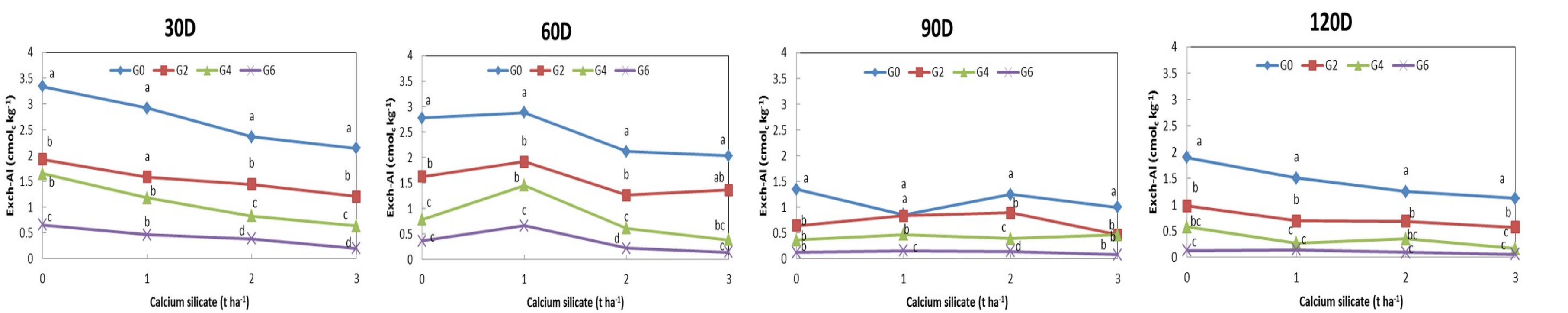
SA: Soil amendments (GML cost at USD 122 t^{-1} and calcium silicate cost at USD 30 t^{-1})

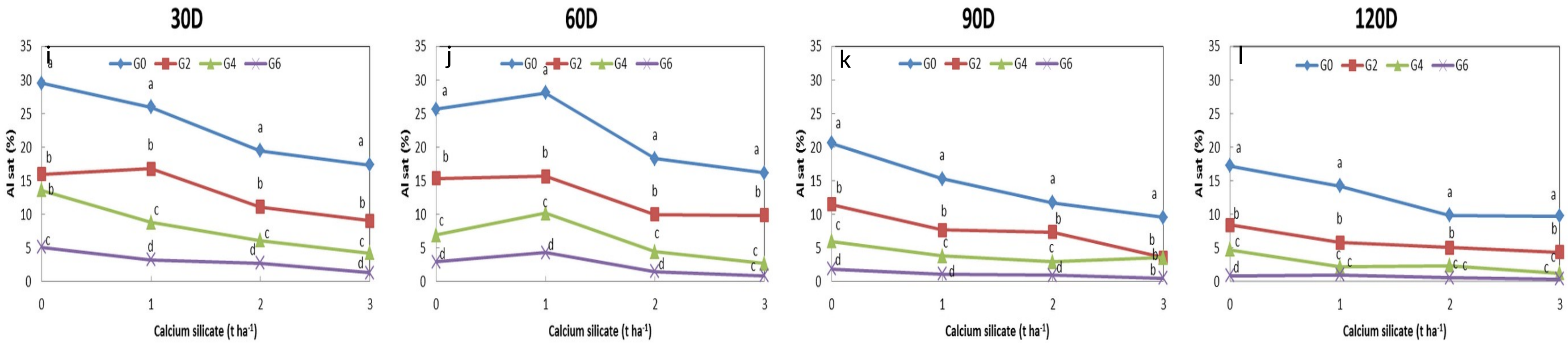
L: Labor cost at USD 45 t^{-1}

T: Total cost of SA+L

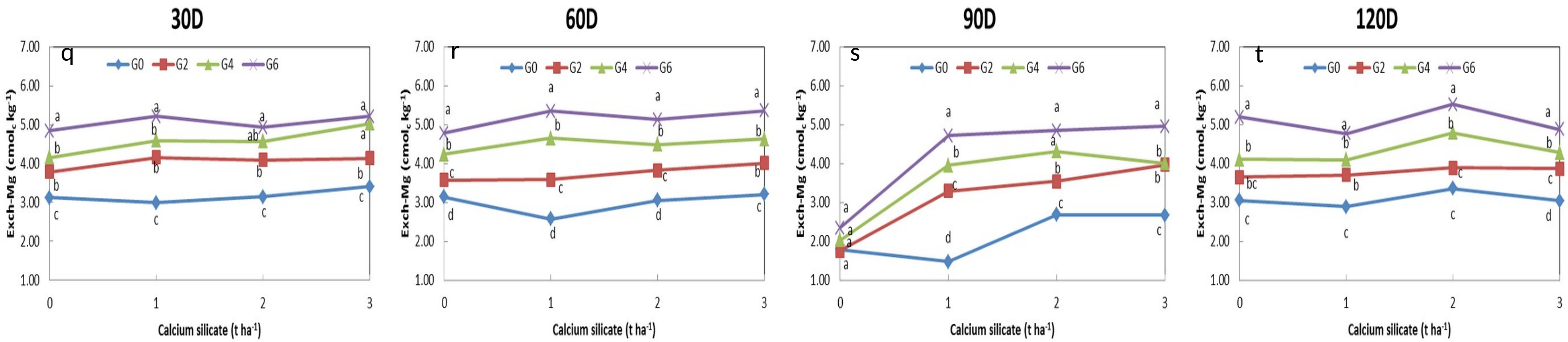

30D
a
60D
b
90D
c
120D
d
G0 G2 G4 G6
Soil pH
Calcium silicate (t ha-1)

e f g h


30D
60D
90D
120D
G0 G2 G4 G6
Exch-Al (cmolc kg-1)
Calcium silicate (t ha-1)


30D
60D
90D
120D
i
j
k
l
G0 G2 G4 G6
Al sat (%)
Calcium silicate (t ha-1)
0
1
2
3
0
5
10
15
20
25
30
35

m n o p


30D
q
60D
r
90D
s
120D
t
G0 G2 G4 G6
Exch-Mg (cmolc kg-1)
Calcium silicate (t ha-1)

u v w x

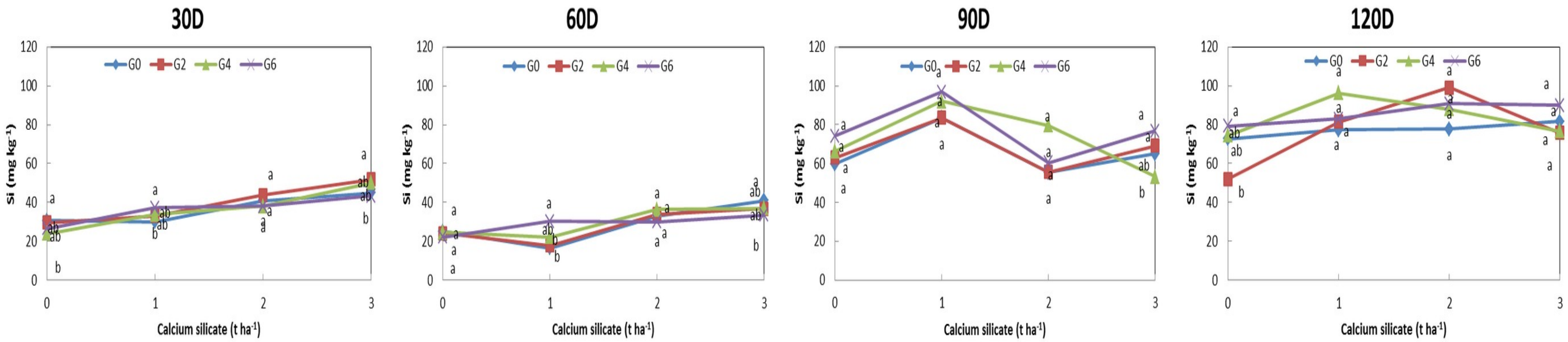


Figure 1. Selected soil chemical properties as an indicator of ameliorative effects under the different rate of calcium silicate incorporated with GML (soil amendments) on acidic soil of rice-cropped soil. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey`s Test). (a-d : soil pH, e-h : exchangeable Al, i-l : Al saturation, m-p : exchangeable Ca, q-t : exchangeable Mg, u-x : Si content).

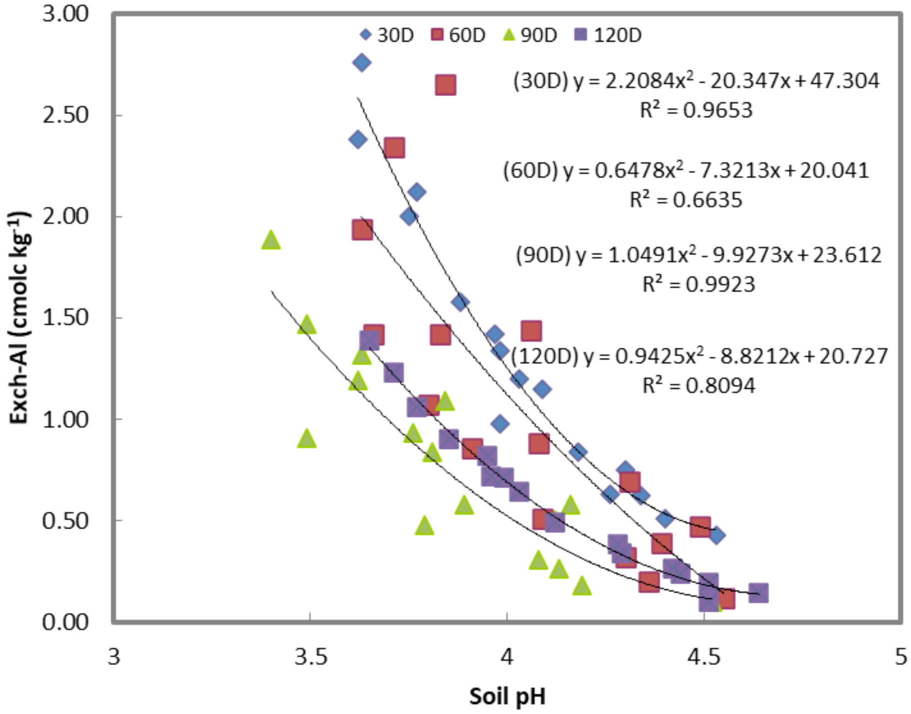
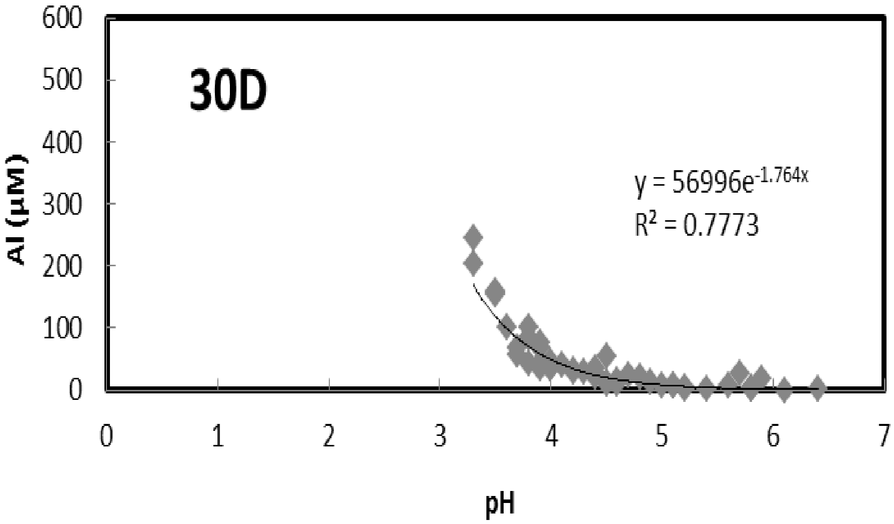
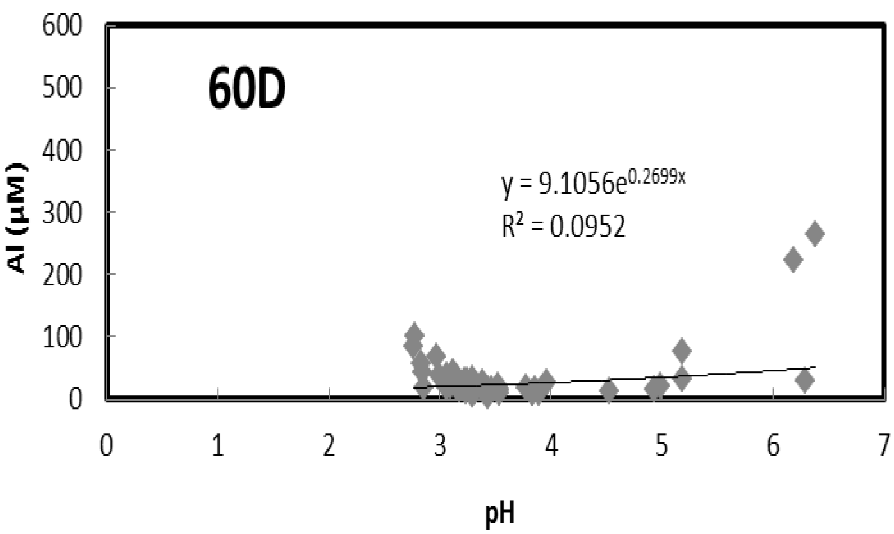


Figure 2. Relationship between exchangeable Al against soil pH on acidic sulfate soil. Polynomial regressions were conducted for the curves.

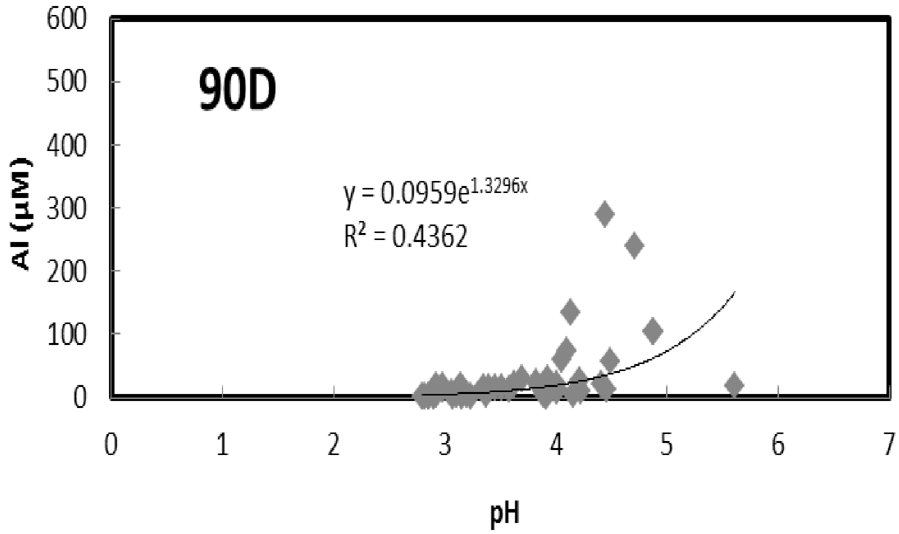
a


30D
y = 56996e-1.764x
R² = 0.7773
Al (µM)
pH
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7

b


60D
y = 9.1056e0.2699x
R² = 0.0952
Al (µM)
pH
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7

c


90D
y = 0.0959e^1.3296x
R² = 0.4362
Al (µM)
pH
0
100
200
300
400
500
600
0
1
2
3
4
5
6
7

d

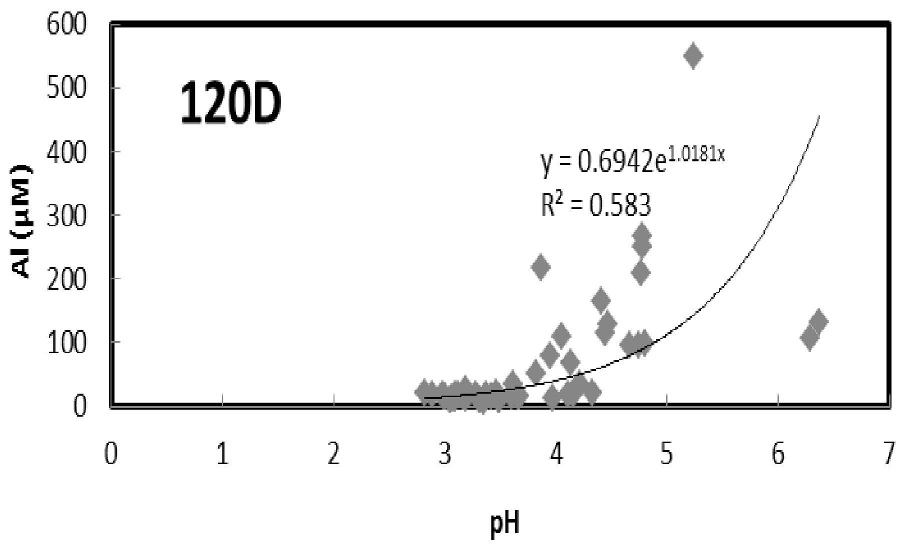
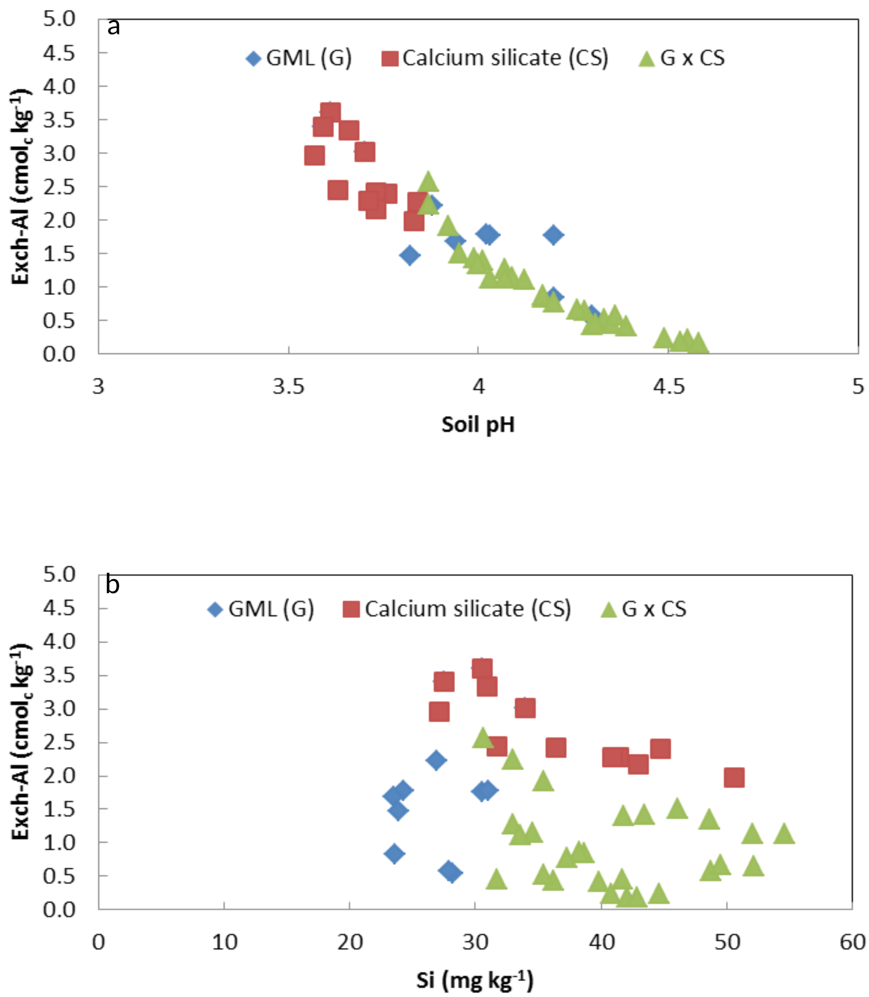
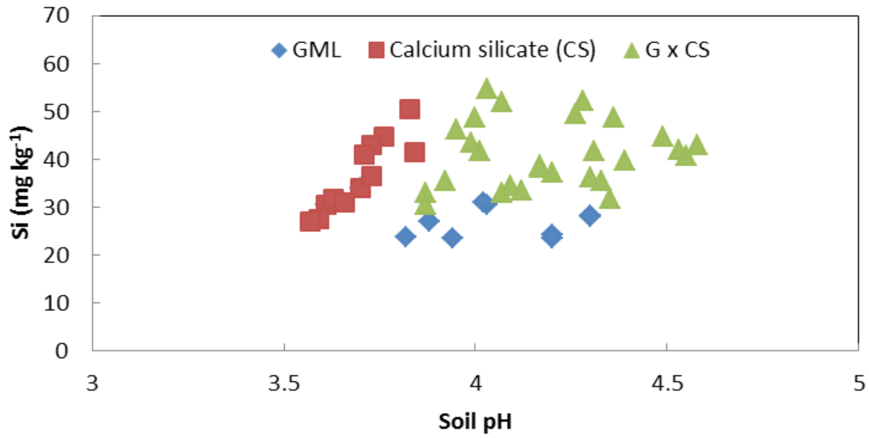

120D
y = 0.6942e^1.0181x
R² = 0.583
Al (µM)
pH
0
100
200
300
400
500
600
0
1
2
3
4
5
6
7

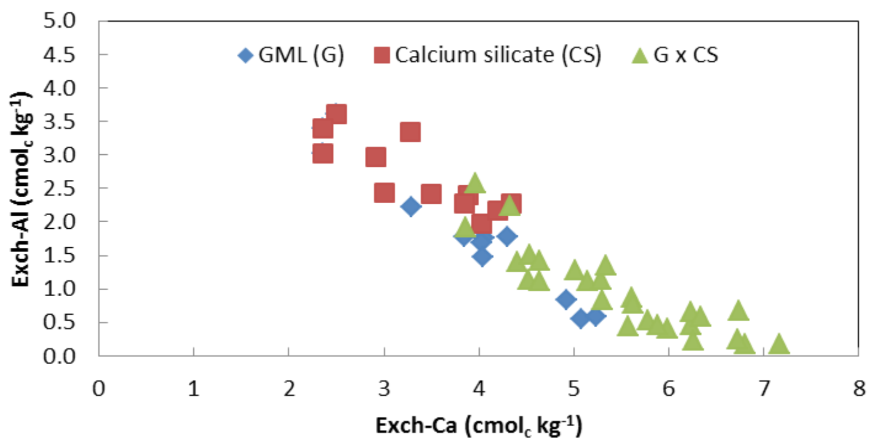
Figure 3. Relationship between Al_{water} concentration and pH of water solution after 30 (a), 60 (b), 90 (d) and 120 (d) incubation period.



c


GML
Calcium silicate (CS)
G x CS
Si (mg kg-1)
Soil pH
0
10
20
30
40
50
60
70
3
3.5
4
4.5
5

d


GML (G)
Calcium silicate (CS)
G x CS
Exch-Al (cmolc kg-1)
Exch-Ca (cmolc kg-1)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
0
1
2
3
4
5
6
7
8

e

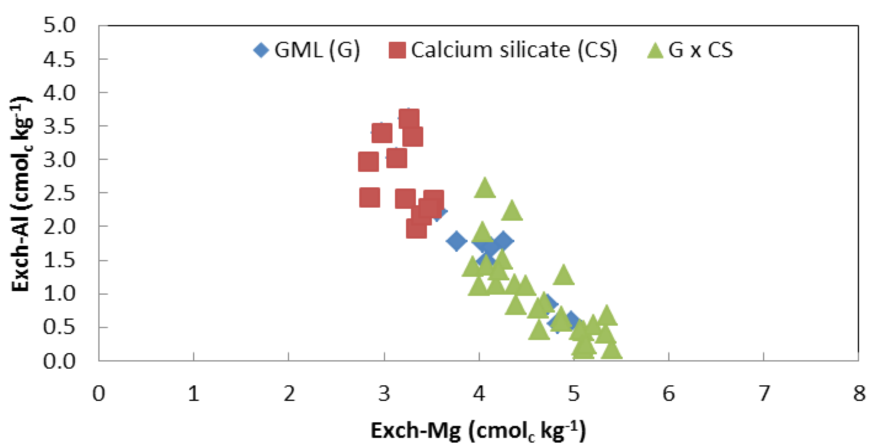

GML (G)
Calcium silicate (CS)
G x CS
Exch-Al (cmolc kg-1)
Exch-Mg (cmolc kg-1)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
0
1
2
3
4
5
6
7
8

Figure 4. Relationship between exchangeable Al and soil pH (a), exchangeable Al and Si content (b), Si and soil pH (c), exchangeable Al and exchangeable Ca (d) and exchangeable Al and exchangeable Mg (e) at the 30th day of the incubation. Dotted lines indicate the critical value of soil chemical parameter.