

博士論文

**Alleviating soil acidity for rice grown with application of soil amendments and its effect on GHG
emissions**

- Finding recommendations for rice production in Malaysian acid soil

(土壌改良剤による水田土壌酸性度の改善と温室効果ガス排出への影響

-マレーシア酸性土壌における水田作への提言)

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Dedicated to my father Azman Bin Omar and my mother Zainab Binti Husin

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LIST OF ABBREVIATIONS

AA	Auto analyzer
AAS	Atomic absorption spectrophotometer
ANOVA	Analysis of Variance
CEC	Cation Exchange Capacity
CRD	Completely Randomized Design
DAS	Days after seeding
GML	Ground Magnesium Limestone
LSD	Least significant different
MR	Malaysia Variety
RCBD	Randomized Completely Block Design
SAS	Statistical Analysis Software
SSF	Silicate slag fertilizer
SSL	Self-Sufficiency Level
HL	Hydrated lime
LL	Liquid lime
TN	Total nitrogen
TC	Total carbon
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy

Chapter 1 Introduction

1.1 Research background

Soils in Malaysia are highly weathered with low pH ($\text{pH} < 5$), and low macro- (N, P, K, Ca, Mg etc.) and micronutrients (Mn, Zn, Fe etc.) which are not suitable for rice production. The soils are classified as Ultisols and Oxisols, and categorized as acidic soils with $\text{pH} < 5$. Highly weathered soils such as Ultisol and Oxisol are often deficient in available Si due to extensive leaching processes (Crooks and Prentice, 2012). In Malaysia, these soils are used for rice cultivation, and an average yields of $3.7 \text{ t ha}^{-1} \text{ season}^{-1}$ was recorded in 1995 (Najim et al., 2007). Rice is a staple food in Malaysia, and the Malaysian government acknowledges the need to achieve 100% self-sufficiency level in paddy production in 2020 (<http://www.riceoutlook.com/?s=malaysia>). Therefore, we need to produce more rice than ever before. Rice production can be increased by increasing the area of the rice production or increasing the yield per unit area. With no expansion in area and slowdown in the increase of the yield per unit, the growth of rice production has fallen below the market demand (Shamshuddin et al., 2016).

Land available for agriculture is becoming limited by industrialization, urbanization, and expansion of residential areas so that the need arises to maximize land productivity (Siwar et al., 2014; Najim et al., 2007). Fatimah et al. (2011) revealed that the reduction in paddy area was expected due to the conversion of the paddy area to other agricultural and non-agricultural activities. Thus, one of the possible challenges is to maximally utilize acidic sulfate soils where the crop productivity is comparatively low. Acidic sulfate soil occupies almost 50 million ha worldwide, including Southeast Asia, Australia, West Africa, and Scandinavia (Ljung et al., 2009). In Malaysia, this kind of soil was estimated to cover approximately 0.5 million ha, with 110,000 ha in the Malay Peninsula (Poon and Bloomfield, 1977). Acid sulfate soils are widespread in Malaysia, occurring almost exclusively along the coastal plains (Shamshuddin and Auxtero, 1991; Shamshuddin et al., 1995; Muhrizal et al., 2006; Enio et al., 2011). Around 20,000 ha were being used for rice cultivation in the Malaysian Peninsula (Shamshuddin et al., 2016).

Acidic sulfate soils are dominated by pyrite (FeS_2) and have markedly high acidity (soil $\text{pH} < 3.5$). These soils are produced when the pyrite-laden soils in the coastal plains are opened up for crop production and/or development. This scenario leads to the release of large quantities of Al into the environment (Shamshuddin et al., 2004), which affects crop growth, including oil palm (Auxtero and Shamshuddin, 1991) and cocoa (Shamshuddin et al., 2004), and results in the death of plants and aquatic life in surrounding areas. The major agronomic problems common to acid sulfate soils are toxicity due to the presence of Al, decrease of phosphorous (P) availability, nutrient deficiencies, and Fe (II) toxicity (Dent, 1986; Shamshuddin and Auxtero, 1991; Shamshuddin, 2006).

Aluminium is an important component of the Earth's crust and the third most abundant element after oxygen and silicon. Plant roots are, therefore, almost always exposed to Al in some form. Fortunately, most of this Al occurs as harmless oxides and aluminosilicates. However, when soils become acidic as a result of natural processes or due to human intervention, Al is solubilized into the toxic trivalent cation, Al^{3+} . This form of Al is the most common species present under acidic conditions (Shamshuddin et al., 2010). Kochian et al. (2005) found that in soils with $\text{pH} < 5$, toxic forms of Al are solubilized into the soil solution, inhibiting root growth. Aluminium toxicity has been recognized as a major threat to crop production in the tropics, such as corn (Shamshuddin et al., 1991; Ismail et al., 1993), cocoa (Shamshuddin et al., 2004), and oil palm (Auxtero and Shamshuddin, 1991), which are grown on moderately to very acidic soils in Malaysia.

Generally, acidic sulfate soils are unsuitable for crop production, unless they are properly ameliorated. Application of soil amendments is a common approach to alleviate soil acidity and to improve its fertility. In Malaysia, some soil amendment practices such as the application of ground magnesium lime (GML), hydrated lime, liquid lime, basalt, organic matter, and/or combinations at appropriate rates for rice crop production in acidic soil, are in place (Ting et al., 1993; Muhrizal et al., 2003; Muhrizal et al., 2006; Suswanto et al., 2007; Shazana et al., 2013; Elisa et al., 2014; Rosilawati et al., 2014; Shazana et al., 2014).

Lime application, in the form of ground magnesium lime (GML) in rice production, is the general practice and it is available locally in Malaysia. Department of Agriculture Malaysia, Ministry of Agriculture (2006) suggested farmers to use lime at the rate between 1.5 to 5 t ha⁻¹ of GML for rice cultivation based on soil acidity. Higher acidity soil requires a greater amount of GML to neutralize the soil acidity. Liming is the common approach used to raise pH. By increasing soil pH to > 5, soluble Al often precipitates in soil as gibbsite (Al (OH)₃). Thereby Al reduces its toxicity in soil. While increasing soil pH, GML can also supply a large quantity of Ca and Mg for crop uptake. Both of them are essential nutrients for optimal rice growth. A study by Shazana et al. (2013) and Shamshuddin et al. (2013) found that application of 4 t ha⁻¹ GML was able to produce a rice yield of up to 4.2 t ha⁻¹ season⁻¹ and 9.8 t ha⁻¹ year⁻¹ in the Kelantan area. Furthermore, Ting et al. (1993) stated that rice yield increased from < 2 to 4.5 t ha⁻¹ season⁻¹ after annual GML application of 2 t ha⁻¹ in the Merbuk, Kedah area. In addition, Panhwar et al. (2014) recorded that application 4 t ha⁻¹ of GML increased in rice grains weight pot⁻¹ by 82.71% over control (without soil amendments).

Global warming, due to the increase of greenhouse gases (GHG), has recently become more serious, and paddy fields are known to be a major source of GHG emissions. Among the greenhouse gases, methane (CH₄) and nitrous oxide (N₂O) are the most important due to their radiative effects, as well as global warming potentials (GWPs) (IPCC, 1995). Wetland rice agriculture is an important source of CH₄ that accounts for approximately 20%–26% of the global anthropogenic methane emissions to the atmosphere (Neue and Roger, 1993). The global average CH₄ emission from rice cultivation is approximately 60 Tg GH₄ year⁻¹, ranging from 20 to 150 Tg CH₄ year⁻¹ (Prinn 1994; Husin et al., 1995), and these emissions may increase further due to expansion of rice cultivation and over-intensification of rice agriculture to cater for the expanding world population (Singh and Singh, 1995). The production and consumption of soil greenhouse gases (GHG) are mediated by several microbial processes (Conrad, 1996). For instance, soil carbon dioxide (CO₂) emissions are the result of microbial heterotrophic respiration. Methane (CH₄) is normally oxidized by methanotrophic prokaryotes in soils (Goulding et al., 1995), whereas soil nitrous oxide (N₂O) production is the result of nitrification and denitrification processes (Poth and Focht, 1985; Daniel Plaza-Bonilla et al., 2014). Environmental factors in the field (Huang et al., 2002; Fey and Conrad, 2000), water regimes (Watanabe

et al., 1995; Wassmann et al., 2000; Xiong et al., 2007), fertilizer management (Cai et al., 1997; Minami, 1995), and organic amendment (Watanabe et al., 1995; Zou et al., 2005) have been identified as determinative factors for CH₄ and N₂O emissions.

Calcium silicate slag fertilizers have been used widely in agriculture in many countries (Japan, United State, China etc.), for rice, sugarcane, and corn, because they provide adequate silicate ions, necessary for higher rice productivity (Ma et al., 1989), and for inducing resistance to biotic (disease and pest) and abiotic stress (Takahashi et al., 1990). Among the abiotic stresses, metal toxicity, nutrient imbalance, salt stress, extreme temperatures, radiation, and drought have been verified in a wide variety of plant species (Bowen et al., 1992; Menzies et al., 1992; Kay et al., 1998; Datnoff et al., 2001; Hattori et al., 2005; Ma, 2004).

Application of silicon-rich materials effectively reduced the Al toxicity in plants through the reduced uptake of Al (Haak and Siman, 1992; Hammond et al., 1995; Myhr and Estad, 1996; Wang et al., 2004). The potential mechanisms for this effect include the following: 1) the precipitation of Al caused by the increased soil pH as a result of elevated concentration of H₄SiO₄ (Lindsay, 1979); 2) the H₄SiO₄ was adsorbed on Al hydroxides, which formed a less mobile compound and diminished the activity of the phytotoxic Al in solution (Panov et al., 1982; Baylis et al., 1994); and 3) the mobile Al was strongly adsorbed on silica surfaces (Schulthess and Tokunaga, 1996). The reduction in Al toxicity to plants was not caused entirely by the immobilization of Al in the soil or growth media, Rahman et al. (1998) reported that an increase in silicon nutrition increases the tolerance of plant to excessive amounts of absorbed Al.

Fundamental countermeasures proposed to date are to maintain the plow layer in an oxidative condition to decrease CH₄ emission from paddy fields (Yagi and Minami, 1990). After submerging, the level of soil reduction is dependent on the amount of oxidizing agents existing in the soil. Iron oxide is considered to function as a major oxidizing material, which controls the production of CH₄ (Watanabe and Kimura, 1999) under submerged conditions. Application of amorphous iron oxide in rice paddy soils (Asami and Takai, 1970; Inubushi et al., 1997; Yoshiba et al., 1996) is not feasible for mitigating CH₄ emission due to the fact that amorphous iron oxide is too expensive for field application. Alternatively, calcium silicate slag is an economically feasible at the field level which is a by-product

of steel industry and contains high amount of active iron oxide, could be used as an oxidizing agent in rice farming (Ali et al., 2008; Ali et al., 2012; Chang Hoon Lee et al., 2012). Silicate fertilization and phospho-gypsum application along with nitrogenous fertilizer in rice farming significantly decreased seasonal CH₄ flux by 16%–20% and increased rice productivity by 13%–18% in Korean paddy soil (Ali et al., 2008), whereas a 12%–21% reduction in total seasonal CH₄ flux and 5%–18% increase in rice grain yield was recorded through silicate fertilization with urea application in the upland rice paddy soils of Bangladesh (Ali et al., 2012).

1.2 Justification and objectives of the study

As stated above, the Malaysian Governments has a policy to achieve 100% self-sufficiency level (SSL) in paddy production by 2020 (<http://www.riceoutlook.com/?s=malaysia>) as the staple food of the country. To increase the SSL, there are three possible alternatives: 1) expanding the rice cultivation area; 2) increasing the yield per unit area, and/or; 3) a combination of 1 and 2. At present, with the scarcity of suitable fertile land, minimal expansion of rice areas can be expected, resulting in the slow increase in rice yield (Siwar et al., 2014; Fatimah et al., 2011; Najim et al., 2007). Because, in reality, the rice production in Malaysia is not sufficient to demand in reality, farmers need to increase their rice production even on land considered to be less fertile such as acid sulfate soils. These soils have low pH (< 4) and high Al content ($> 2 \text{ cmol}_c \text{ kg}^{-1}$), which can be detrimental to crop production. Generally, pH values below 4 reduce root growth (Arnon et al., 1942; Islam et al., 1980) while critical level of Al is $< 2 \text{ cmol}_c \text{ kg}^{-1}$ (Hiradate et al., 2007).

In Malaysia, acid sulfate soils were estimated to cover about 0.5 million ha area with 110,000 ha in the Malay Peninsular (Poon and Bloomfield, 1977). Around 20,000 ha were being used for rice cultivation in Peninsular Malaysia (Shamshuddin et al., 2016). This soil occurs exclusively in the coastal plains (Shamshuddin et al., 1995; Muhrizal et al., 2006; Enio et al., 2011). This soil produces high acidity when the soil is opened up for development. As a result, high amount of Al was released into the environment (Shamshuddin et al., 2004), affecting rice growth (Ting et al., 1993).

To improve the fertility of acidic sulfate soil in Malaysia, application of GML is commonly used by farmers to reduce soil acidity in Malaysia. Department of Agriculture Malaysia, Ministry of Agriculture (2006) suggests GML application of $1.5 - 5 \text{ t ha}^{-1}$ based on soil acidity. High soil acidity requires high amount of GML to neutralize the soil acidity. In the case of acid sulfate soil with high acidity (low pH and high Al content), GML was required at 4 t ha^{-1} and above to increase the soil pH at least at 4 and above (Payman Hassan et al., 2016; Shamshuddin et al., 2016; Shamshuddin et al., 2013; Panhwar et al., 2014).

However, because the price of GML has been rapidly increasing and its improving effects on acid sulfate soil is limited, a less costly and more effective alternative way of soil amendment application is highly required by the farmers. For example, the price in 2010 is USD 50 t⁻¹ while in 2016 is USD 122 t⁻¹.

In addition, rice fields are noted as a major source of greenhouse gases emissions (GHG) accelerating the global warming. Methane and nitrous oxide are the most important greenhouse gases due to their radiative effects as well as global warming potentials (GWPs) (IPCC, 1995). Malaysia will require more rice as the Malaysian government aims to increase SSL. Therefore, the rice cultivable area must be expanded to fulfill the desired production target, which may significantly accelerate CH₄ and N₂O gas emissions. Thereby, we expect that the soil amendment to mitigate the emission will be also required.

Considering such background of Malaysian rice production, the motivation of this study is to identify soil amendments which can fulfill both of the requirements; (1) less costly and more effective fertility improvement of acidic sulfate soil than that by the current common practice and (2) mitigation of greenhouse gas emission.

Meanwhile, the Environment legislation of Malaysia does not allow us to use a globally and widely used soil amendment, calcium silicate slag which is a by-product from iron industries. In Malaysia, it is classified under Malaysian law (Environmental Quality Act 1974, First Regulation (Schedule 2)) as SW 104, metal and metal bearing waste. Therefore, it has not been ever used as a soil amendment in Malaysia in spite of its much lower price than that of GML. The disposal of calcium silicate slag is subjected to incineration at USD 1–1.50 kg⁻¹, which is expensive compare to selling price at USD 30 t⁻¹. Such Malaysian situation of calcium silicate slag has not promoted the studies on its use as a soil amendment on acidic sulfate soil in Malaysia and the knowledge on its use for the Malaysia soils is currently rather poor. In this study, we focus on such calcium silicate slag as a possible alternative soil amendment of GML, assuming that calcium silicate can be a candidate to fulfill both of the requirements, considering its chemical characteristics and price. We expect that this study can trigger the change of the policy on calcium silicate slag in Malaysia overcoming the current bad reputation on it, once this study can suggest a better recommendation on the soil amendments for

acidic sulfate soils in Malaysia using calcium silicate slag, than the current common practice. We can also expect that the use of calcium silicate slag will reduce the waste of industries which is one of serious environmental issues in Malaysia.

In addition, we can also expect that adding calcium silicate onto the soil will indirectly facilitate GML to move downwards into the soil (Castro and Crusicol, 2013), resulting in the reduction of GML surface runoff in acidic sulfate soil in Malaysia. Furthermore, we can expect that the movement of calcium silicate downwards into the soil would prevent the pyrite oxidation (Kollias et al., 2014) which normally takes place in the subsoil of acidic sulfate soil. Pyrite oxidation release H^+ ions into the soil system and generally H^+ ions are known to dissolve metals. Hence the prevention of the pyrite oxidation inhibits the production of H^+ ions that leads to the dissolution of metal (i.e Al). Subsequently, we expect that toxicity (i.e Al toxicity) also reduced resulting in less harmful soil for rice growth.

Summarizing the above, this study aims to provide a less costly and more effective recommendation of soil amendments to improve the soil fertility of acidic sulfate soils in Malaysian paddy fields while simultaneously mitigating greenhouse gas emission from the fields. In order to achieve the objectives, we assumed three possible sulfate soil acid fertility improvement ways; (1) reduce the use of GML; (2) identify an alternative soil amendment to GML, or (3) use GML in combination with an alternative soil amendment. Based on the assumption, we designed our study as follows and conducted corresponding experiments;

1. To access the performances and cost-effectiveness of various liming materials commonly used (ground magnesium limestone (GML), hydrated lime (HL), and liquid lime (LL)) to increase rice yield of acidic sulfate soil in Malaysia
2. To evaluate the effect of GML to assess the possibility of reducing current application rate of 4 t ha^{-1} commonly used by farmers to improve the fertility of acid sulfate soil in Malaysia.
3. To evaluate the ameliorative effect of calcium silicate on acidic sulfate soil in Malaysia as an alternative to GML

4. To evaluate the combination effect of GML and calcium silicate on acidic sulfate soil in Malaysia and to determine the optimal combination of them, considering the costs incurred and the positive soil chemical characteristics achieved on acidic sulfate soil
5. To assess the ability for calcium silicate to mitigate emission of greenhouse gases such as methane and nitrous oxide from rice cropped soil.
6. To provide the recommendation rate of GML in-combination with calcium silicate based on;
 - 1) Positive effects on chemical characteristics of acidic soil;
 - ii) The reduction in net GWPs of rice cropped soil;
 - iii) The cost incurred by soil amendments.

Because of the ban on the use of calcium silicate slag in Malaysian soil, we tentatively used chemical calcium silicate in this study in stead.

1.3 Structure of the thesis

The present study consists of 7 chapters with 6 objectives. These studies were conducted on rice-cropped soil of Malaysia and Japan. Field-trial, laboratory, and glasshouse experiments have been conducted in Malaysia for chapter 2, 3, 4 and 5, whereas for chapter 6, further laboratory and glasshouse experiments have been conducted in Japan.

In Chapter 1, the author provides an introduction on the significance of the present study.

Chapter 2 presents to fulfill the objectives 1. This chapter discusses the information given for the selected area characterized by acidic soil in Malaysia, which was planted with rice, along with an assessment of performance and cost-effectiveness of the three investigated amendments (GML, HL, LL) to increase rice yield.

Chapter 3 presents to fulfill the objective 2. This chapter focusses on the common use of GML by farmers in Malaysia. This use was evaluated at a different rate to investigate the possibility of reducing the GML rate currently used by farmers (4 t ha^{-1}).

Chapter 4 presents to fulfill the objective 3. This chapter discusses about the effect of calcium silicate as an alternative soil amendment to alleviate soil acidity in replacement to GML.

In Chapter 5, the recommended rate of GML in combination with calcium silicate is discussed. This chapter presents to fulfill the objective 4. The recommendation has been made based on the positive effects achieved on chemical properties of acidic rice cropped soil in Malaysia, and also the costs incurred.

Besides ameliorating soil acidity and improving soil fertility, the application of calcium silicate was further investigated on its ability in mitigating GHG emissions of rice-cropped soil in Chapter 6 to fulfill the objective 5. This investigation involved two experiments. The first experiment was conducted to investigate the efficacy of calcium silicate on GHG emission, whereas the following experiment was conducted to emphasize the ability of calcium silicate in mitigating nitrous oxide emission of cultivated rice.

Last but not least, Chapter 7 presents:

- 1) A summary of all the results obtained in the present study;
- 2) Conclusions of the present study;
- 3) The recommended rate of the use of GML in combination with calcium silicate for farmers. This part presents to fulfill the objective 6. The recommended rate of GML in combination with calcium silicate are considering on:
 - a) the positive effect on soil chemical characteristic based on the selected guidelines;
 - b) the significant effect of calcium silicate in reducing nett GWPs, and;
 - c) a cost-benefit analysis between GML and SSF (replacement of calcium silicate).
- 4) A recommendation for future research on calcium silicate slag for agriculture purposes.

2.1 Introduction

The demand for the rice consumption of rice worldwide is increasing over the years (Yap, 2012). Therefore, we need to increase rice production. With no expansion in area and the slowdown in yield per area increase, the growth of rice production has fallen below market demand in Malaysia (Shamshuddin et al., 2016). The use of marginal land is an option to increase rice yield. One of the soils targeted is acid sulfate soil. Acid sulfate soils is not suitable for crop production without proper amelioration (i.e., liming the soil) measures in place. Liming is a common approach to improve acidic soil prior to crop production, and in Malaysia, various liming materials are available locally, whereas some are imported. Britestone Sdn. Bhd is one example of a local liming material company. This company mines limestone from the limestone hills of Ipoh, Perak, west coast of Peninsular Malaysia. Liming raises soil pH so as to precipitate Al as inert Al-hydroxides, thereby reducing its toxicity (Shamshuddin et al., 2010). Besides, increasing pH, GML can supply Ca and Mg. According to Ting et al. (1993), rice could achieve a yield of 4.5 t ha⁻¹ season⁻¹ due to annual GML application of 2 t ha⁻¹. A past study by Shamshuddin et al. (1998) found that application of 4 t ha⁻¹ GML showed a beneficial effect lasted for eight years with the effect being comparable to application of 1 t ha⁻¹ GML annually..

In Malaysia, the most common liming material used by rice farmers within acid sulfate soil areas is hydrated lime (Ca(OH)₂). According to the farmers, hydrated lime shows immediate effect upon application to the soil; therefore, they apply hydrated lime every season prior to rice planting.

In addition, liquid lime (liming material) was introduced by Humibox (M) Sdn. Bhd., a private company. The company claims that the application of lime in a liquid form is more effective in correcting soil acidity compared with the powder form (<http://www.humibox.com/products/soil-acidity-correctors/liquid-lime>). The field trials were conducted in Seberang Perak area and the rice yield increased by 28.5% after applied with liquid lime in 2004 compared to 2003 (unpublished).

Undeniably, application of effective liming material is necessary to improve the infertility of acidic soil for crop production. Therefore, the objective of this study was to access the performances and cost-effectiveness of various liming materials commonly used (ground magnesium limestone (GML), hydrated lime (HL), and liquid lime (LL)) to increase rice yield of acidic soil in Malaysia.

2.2 Materials and methods

2.2.1 Study site description

The present study was conducted in Merbok Kedah, Malaysia (5.7185 N, 100.3812 E) (Figure 2.1 and 2.2). The planned agricultural area with acidic soil was approximately 3,000 ha. The main crop grown in this area is rice, with an average yield $< 2 \text{ t ha}^{-1} \text{ season}^{-1}$. Generally, rice is cultivated twice a year; however, some areas are only able to support a single cultivation per year. Of noteworthiness is that these areas have no irrigation and drainage systems. Therefore, farmers rely solely on rain watering (rain-fed condition). In addition, rice grown in this area is often exposed to severe infections by *Magnaporthe grisea* (*M. grisea*), a fungal disease more commonly known as rice blast, which unfortunately further reduces rice yield (Figure 2.3).

At the onset of the current experiment, soils were sampled at 15 cm intervals to a depth of 75 cm at selected locations in the experimental plots to determine the soil natural chemical properties (Table 2.1). The soil composition was clay loam with 31.25% sand, 39.36% silt, and 29.18% clay.

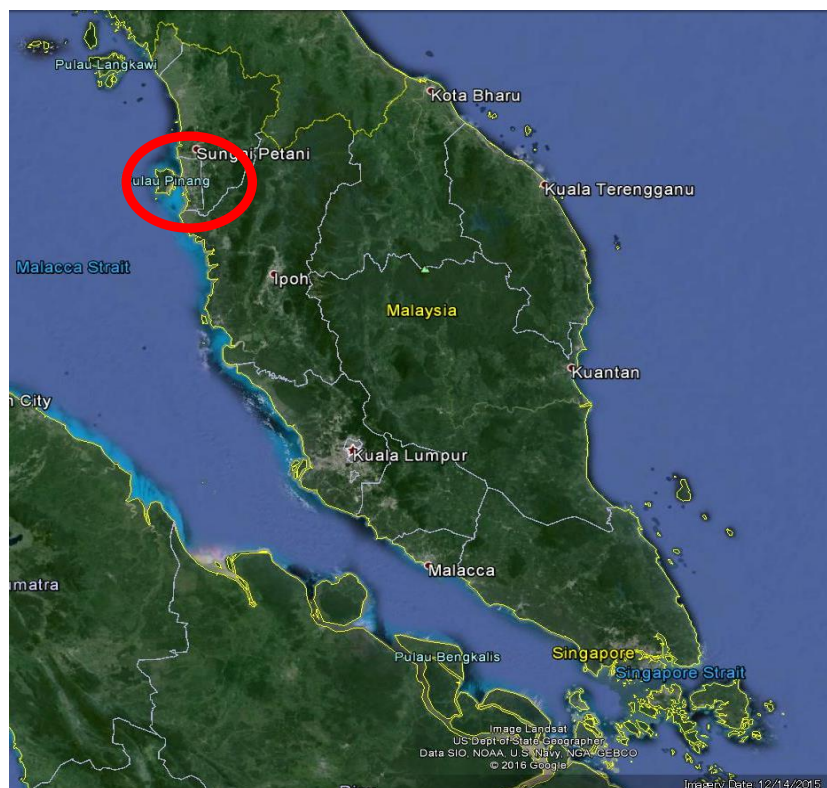


Figure 2.1 Satellite photo of Peninsular Malaysia. The study area at northern region of Peninsular Malaysia (red circle). Source: Google earth

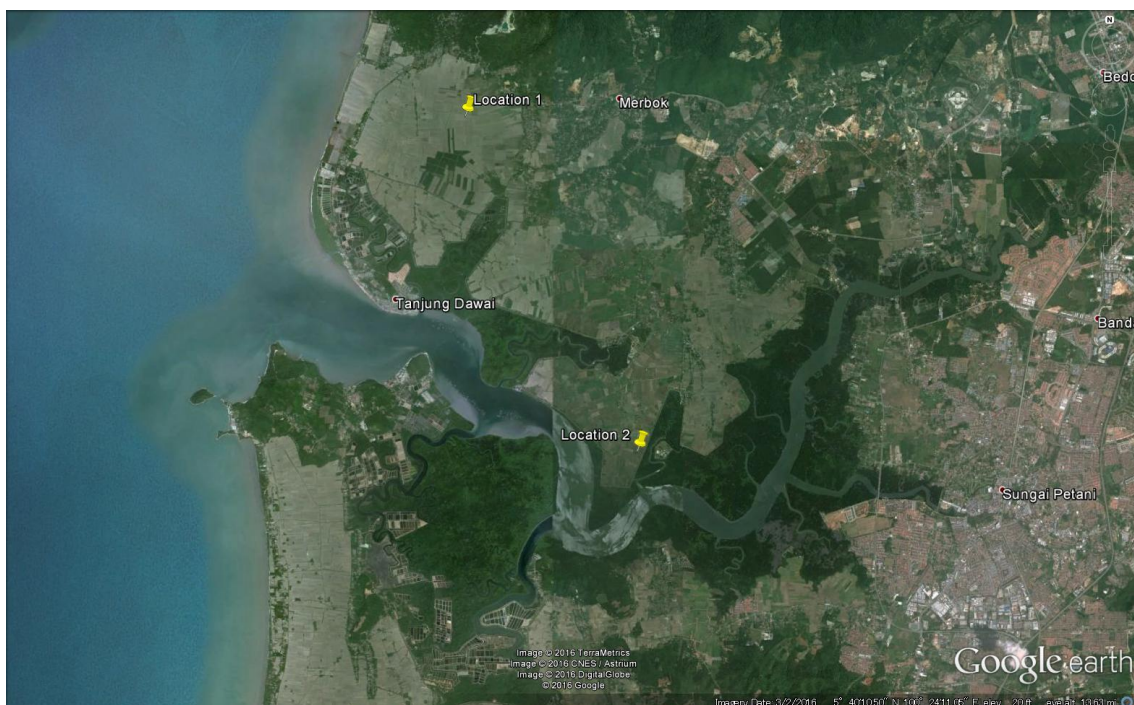


Figure 2.2 Satellite photo indicates Merbok region, Kedah, where the field trial carried out at location 1 (yellow pin). Source: Google earth. Location 1: Singkir Darat.



Figure 2.3 The condition of rice after being attacked by rice blast at 90 DAS

2.2.2 Treatments, experimental design and crop management

The treatments and elemental composition of liming materials used for the current experiment are shown in Table 2.2 and Table 2.3, respectively. The experimental design used was a Randomized Completely Block Design (RCBD) with five replicates. Each experimental unit was 5 m × 5 m in size, and the plots were separated by plastic film (to a depth of 15 cm under the soil surface) to minimize water movement among the experimental plots. Rice was cultivated for two seasons.

Rice seeds were sown (direct seeding) during April and October 2010 for the first and second seasons, respectively. During the first season (April–August, 2010), there was an extended dry period during the vegetative and reproductive phases (Figure 2.4a). Therefore, water needed to be pumped from the nearest canal (acidic water) to ensure that the rice seeds germinated (Figure 2.4b). On the other hand, there was no water limitation during the second season (September 2010–January 2011) due to intermittent heavy rainfall throughout the season (Figure 2.5). The rice crop was harvested during August 2010 and January 2011 for the first and second seasons, respectively.

The rice variety used for this experiment was MR 219 at a rate of 150 kg ha⁻¹. MR 219 is commonly used by the farmers in Peninsular Malaysia. The rice seeds were soaked with seed enhancer (ZAPPA®) for 24 h. Subsequently, the rice seeds were rinsed with tap water and left in the dark for 24 h before sowing in the field. ZAPPA® is specially formulated as a paddy seed treatment to enhance rapid seed germination for direct seeding rice grown under aerobic and anaerobic systems (<http://www.diversatechfertilizer.com/zappa/>, 2015) and is recommended by the Department of Agriculture (Malaysia).

Fertilizer was applied in the experimental plots based on the standard fertilizer rate (120 kg N ha⁻¹, 70 kg P₂O₅ ha⁻¹, 80 kg K₂O ha⁻¹) using urea, NPK Blue (12:12:17+TE), and NPK Green (15:15:15+TE) as a nutrient source.

a



b



Figure 2.4 Dry conditions the first week after sowing (a) water was pumped in from a drainage canal (b) (for 1st season)



Figure 2.5 The experimental field condition during the second season with excess water

Table 2.1**Soil chemical characteristics at different depths prior to rice sowing**

Depth	pH	EC	Exchangeable cations					Fe	CEC	Total	Total	C:N	Available P	Al saturation
(cm)	water	(dS m ⁻¹)	(cmol _c kg ⁻¹)					(mg kg ⁻¹)	(cmol _c kg ⁻¹)	Carbon	Nitrogen	ratio	(mg kg ⁻¹)	(%)
	(1:2.5)									(%)	(%)			
			K	Ca	Mg	Na	Al							
0-15	2.63	0.71	0.46	1.72	1.45	0.49	6.70	525.00	11.14	2.78	0.19	14.63	12.18	61.92
15-30	2.60	1.54	0.15	1.53	1.89	0.52	8.63	284.70	11.35	1.82	0.10	18.20	10.22	67.84
30-45	2.56	1.85	0.18	1.89	2.14	0.55	8.12	316.40	11.93	1.89	0.10	18.90	10.08	63.04
45-60	2.58	2.41	0.18	1.77	2.69	0.73	8.45	307.50	13.35	2.30	0.10	23.00	12.46	61.14
60-75	2.89	5.00	0.19	2.12	3.35	1.07	9.86	560.55	15.57	3.54	0.12	29.50	15.54	59.43

Soil pH was determined in water at the soil to solution ratio of 1:2.5 using a pH meter (Sartorius pH meter PB-11).

EC was determined in water at the soil to solution ratio of 1:5 using an EC meter.

The basic cations (K, Ca, Mg, Na) in the 1 M NH₄OAc solution were determined by atomic absorption spectroscopy (AAS) (Perkin Elmer, model 1100B)

Cation exchange capacity was determined by 1 M NH₄OAc, which was buffered at pH 7

Exchangeable Al was extracted by 1 M KCl, and the Al in the extract was determined by AAS (Perkin Elmer, model 1100B)

Extractable Fe (Dilute Double Acid method) was also determined by AAS (Perkin Elmer, model 1100B).

Total carbon and nitrogen were determined by the CNS Analyzer Leco RC-412 (Leco Corporation, St. Joseph, MI). Available P was determined using Bray II extracting reagent (0.1 N HCl with 0.03 N NH₄F) and was measured by auto-analyser (AA) (Lachat QuickChem® 8000 Series FIA + Syatem; Lachat Instruments, Loveland, USA).

2.2.3 Measurement of rice yield components

Rice was harvested on the 29th August, 2010 and 13th February, 2011 for the first and second seasons, respectively. Paddy crops were harvested in microplots for data analyses, using quadrates of 25 cm × 25 cm in size. The samples were taken to the laboratory for yield component analysis. The following yield components were determined: 1) the panicle number by counting all panicles from each quadrate sampled, and 20 panicles were randomly selected from each experimental plot for further yield component analysis; 2) the panicle length was measured using a ruler; 3) the determination of spikelet per panicle was performed by threshing the grains from the panicles, with a seed separator used to separate unfilled and filled spikelets, and; 4) the percentage of filled spikelets was calculated using a formula (filled spikelets per panicle/ total spikelets per panicle) × 100; and 1,000 grain weight. Grain yield (t/ha) was calculated using this equation proposed by Yoshida (1981):

$$Y = N \times W \times F \times 10^{-5}, \quad (\text{Equation 1})$$

Where Y = grain yield (t ha⁻¹), N = spikelet number m⁻², W = 1,000 grain weight (g), and F = filled spikelets (%).

Equation 1 was used for data determination; however, during the second season of the study, the paddy crop was unfortunately infected with rice blast disease (Figure 2.3).

Table 2.2
Various liming materials used for the rice cultivation experiment

Symbol	Treatments
T1	Control (no liming material)
T2	^a Ground magnesium limestone (GML) (4 t ha ⁻¹)
T3	^a Hydrated lime (2 t ha ⁻¹)
T4	^b Liquid lime (applied only for first season) (20 L ha ⁻¹)
T5	^b Liquid lime (applied only for first and second season) (20 L ha ⁻¹)
T6	^a Hydrated lime (no fertilizer applied) (2 t ha ⁻¹)

^a Applied one month prior rice seeding

^b applied one day prior rice seeding

Table 2.3**Elemental composition of various liming materials used for the rice cultivation**

Elemental composition	Ground magnesium limestone (GML)	Hydrated lime (HL)	Liquid lime (LL)
pH	8.93	9-10	9.1
CaO (%)	31-38	65	99% as CaCO ₃
MgO (%)	15-18	n.a	0.2
SiO ₂ (%)	< 0.2	n.a	n.a
Fe ₂ O ₃ (%)	< 0.2	n.a	n.a
Al ₂ O ₃ (%)	n.a	n.a	n.a
Particle size	100% passing thru a 20 mesh screen, 70% passing thru a 100 mesh screen and > 40% passing thru 200 mesh screen.	200 mesh size	1.5-5 µm
Chemical formula	CaMg (CO ₃) ₂	Ca (OH) ₂	CaCO ₃
Calcium carbonate equivalent	109	135	100

2.2.4 Soil sampling and soil analyses

Soil sampling was conducted twice during the experiment: at the harvests of the two seasons. Only topsoil (0–15 cm) was sampled from each experimental plot using a soil auger. 3 samples were taken from each plot. A total of 180 soil samples were collected (6 treatments x 5 replicates x 2 seasons x 3 samples each plot). The samples were air dried, ground, and filtered through a 10-mesh sieve (2 mm).

Soil pH was determined in water at the soil to solution ratio of 1:2.5 using a pH meter (Sartorius pH meter PB-11), whereas electrical conductivity (EC) was determined in water at the soil to solution ratio of 1:5 using an EC meter. The basic cations (Ca, Mg, K, Na) in the 1 M NH_4OAc solution were determined by atomic absorption spectroscopy (AAS) (Perkin Elmer, model 1100B) instrument. Cation exchange capacity was determined by 1 M NH_4OAc , which was buffered at pH 7. Exchangeable Al was extracted by 1 M KCl, and the Al in the extract was determined by AAS (Perkin Elmer, model 1100B) instrument. Iron in the soils was determined by double acid method. It was extracted using 0.05 M HCl in 0.0125 M H_2SO_4 . Five g of air-dried soil was mixed with 25 mL extracting solution, shaken for 15 minutes and centrifuged at 180 rpm. The supernatant was then filtered through filter paper (Whatman No. 42) and the Fe was analyzed using AAS (Perkin Elmer, mode; 1100B). Total carbon and nitrogen were determined by the CNS Analyzer Leco RC-412 (Leco Corporation, St. Joseph, MI). Available P was determined by the method of Bray and Kurtz (1945) using Bray II extracting reagent (0.1 N HCl with 0.03 N NH_4F). Phosphorus (P) was measured by auto-analyser (AA) (Lachat QuickChem® 8000 Series FIA + Syatem; Lachat Instruments, Loveland, USA).

2.2.5 Plant analyses

Each plant was cut 5 cm from soil surface and oven-dried at 65 °C for three days. The samples were ground (< 1 mm) using MF10 basic microfine grinder (IKA-Werke, Staufen, Germany). Approximately 0.25 g of plant samples were digested by wet-ashing using a 1:1 ratio $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ on a block digester at 350 °C. The digested solutions were diluted using distilled water and filtered through Whatman filter paper No. 42 and made up to a 100 mL volume. The concentrations of calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe) were measured using a AAS Perkin-Elmer AAnalyst 400. Nitrogen (N) and potassium (K) were measured using auto-analyser (AA) (Lachat QuickChem® 8000 Series FIA + Syatem; Lachat Instruments, Loveland, USA).

2.2.6 Water analyses

Water samples (flood water) were collected on a weekly basis from each experimental plot from seeding until harvesting. During the first season, water sampling was started at 14 days after sowing (DAS) due to dry conditions at 7 DAS, whereas for the second season, water was sampled until 77 DAS due to drying up of the paddy field. The water samples were filtered using filter paper. The pH was determined using a Sartorius pH meter PB-11. Aluminum (Al) and Iron (Fe) concentrations were determined using a AAS (Perkin Elmer, model 1100B).

2.2.7 Statistical analyses

Data from the experiment were analyzed using Analysis of Variance (ANOVA), and a Tukey test was employed to determine the mean differences between treatments. The statistical package used was SAS v 9.1 software.

2.3 Results

2.3.1 Soil chemical properties of the experimental plot prior to rice planting

Soil chemical properties prior to the experiment are shown in Table 2.1. Soil pH for topsoil (0–15 cm) indicated high acidity with a $\text{pH} < 3$, whereas exchangeable Al ($6.7 \text{ cmol}_c \text{ kg}^{-1}$) exceeded the critical Al level for rice growth ($2 \text{ cmol}_c \text{ kg}^{-1}$) according to Dobermann and Fairhurst (2000) and Syuntaro et al. (2007). Soil pH decreased with soil depth, whereas exchangeable Al increased with soil depth. Soil pH values clearly indicated high soil acidity within the studied areas. Exchangeable calcium (Ca) was relatively low compared to the minimal requirement of Ca for rice growth at $2 \text{ cmol}_c \text{ kg}^{-1}$ (Table 2.1), according to Palhares de Melo et al. (2001). In contrast, magnesium (Mg) met the Mg requirement of $1 \text{ cmol}_c \text{ kg}^{-1}$ for rice plants as stated by Dobermann and Fairhurst (2000). It is clear that both Ca and Mg increased with soil depth. Total nitrogen (TN) was low. Total carbon (TC) was above 2%, thereby providing a C:N ratio of between 14.6–32.5, sufficient to support microbial activity in the root-rhizosphere system. The higher carbon content of these soils can be attributed to the residual effect of *in-situ* rice straw decomposition after each harvest. Available P was noted to be sufficient, within the $7\text{--}20 \text{ mg kg}^{-1}$ P for rice growth according to Dobermann and Fairhurst (2000).

2.3.2 Rice yield components analyses

During the first rice-season, the yield ranged from 179 g m^{-2} to 371 g m^{-2} , whereas for the second rice-season, the yield ranged from 321 g m^{-2} to 429 g m^{-2} . A significant difference was observed in rice yield among treatments during the first season: 1) the rice yield for soil treated with 4 t ha^{-1} GML was significantly higher than soil treated with liquid lime; 2) soil treated with hydrated lime and ground magnesium limestone showed significant effects compared to untreated soil and liquid lime treatments on 1,000 grain weight. A significant effect was observed between the two seasons of rice cultivation for tillers number (1 m^2), 1,000 grain weight (g), spikelets per panicle, and percentage filled spikelets. The excess of water in the experimental plots (during seeding) may have promoted rice plant growth. This effect was observed in significantly lower tillers number during the second season. During the second season, no significant effects were found for rice yield and rice yield components among treatments. The rice yield increased by 21.21% to 49.15% during the second season.

Table 2.4**Rice yield components for two cultivation seasons**

Season	Treatments	Tillers number (m ⁻²)	# Spikelet per panicle	% filled grains	1000 grain weight (g)	grain yield (g m ⁻²)
1 st season						
S1	T1	198 ^a	119 ^a	47.79 ^{ab}	23.00 ^b	271 ^{ab}
S1	T2	228 ^a	131 ^a	48.43 ^{ab}	25.31 ^a	371 ^a
S1	T3	216 ^a	118 ^a	53.26 ^a	24.70 ^a	338 ^{ab}
S1	T4	190 ^a	100 ^a	40.62 ^b	22.80 ^b	179 ^b
S1	T5	207 ^a	103 ^a	41.60 ^{ab}	22.36 ^b	197 ^b
S1	T6	226 ^a	111 ^a	51.78 ^{ab}	24.99 ^a	326 ^{ab}
2 nd season						
S2	T1	152 ^a	144 ^a	71.46 ^a	24.89 ^a	395 ^a
S2	T2	169 ^a	153 ^a	71.57 ^a	24.24 ^a	434 ^a
S2	T3	168 ^a	149 ^a	68.52 ^a	24.89 ^a	429 ^a
S2	T4	151 ^a	134 ^a	70.58 ^a	25.12 ^a	352 ^a
S2	T5	164 ^a	131 ^a	68.62 ^a	24.90 ^a	368 ^a
S2	T6	161 ^a	126 ^a	63.12 ^a	24.90 ^a	321 ^a

Means marked with the same letter for each season were not significantly different at $p < 0.05$ (Tukey's test)

2.3.3 Soil pH and selected soil chemical characteristics

Soil pH of the topsoil was 2.63 prior to rice planting. Figure 2.6 shows soil pH of the first season and in second season. The soil pH ranged from 2.99 to 3.36 during the first season and 3.07 to 3.33 during second season. After the normal rice cultivation practice for the first season of the experimental study, the sites were applied with the respective (Table 2.2) liming treatments. During the first season, the soil treated with 2 t ha⁻¹ hydrated lime showed a significant increment of soil pH compared to soil treated with 20 L ha⁻¹ liquid lime. Meanwhile, for the second season, the soil pH of the soil treated with 4 t ha⁻¹ was increased significantly compared to soil treated with 20 L ha⁻¹ liquid lime (two seasons).

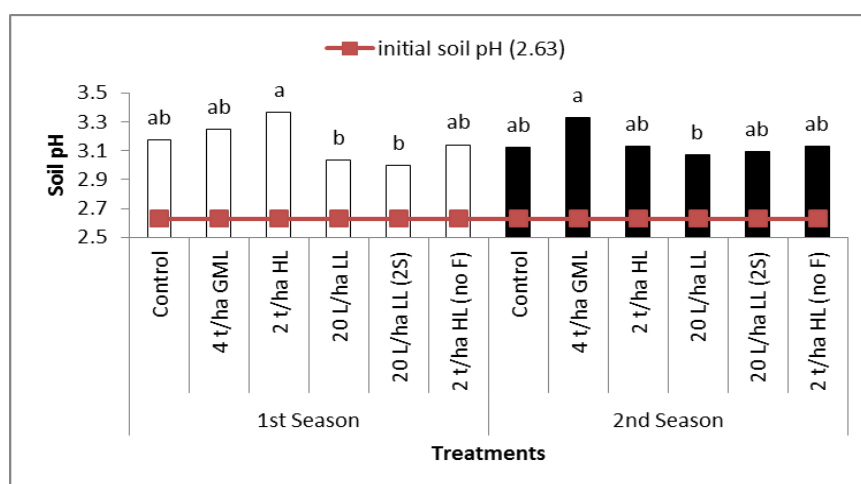


Figure 2.6 Effect of treatments on soil pH. Means marked with the same letter for each season were not significantly different at $p < 0.05$ (Tukey's test)

*GML: ground magnesium limestone

*HL: hydrated lime

*LL: liquid lime

*2S: apply on both seasons

*no F: No fertilizer applied

No significant effect for exchangeable Al was noted among treatments after the first and second seasons of rice cultivation. However, the exchangeable Al after the second season harvest decreased compared to the first season. The reductions in exchangeable Al were between 7.43% to 21.55% for all treatments, except for the soil treated with 2 t ha⁻¹ hydrated lime without fertilizer application. In addition, there was no significant effect among treatments for Fe, available P, total C, and total N after the first and second seasons, as shown in Table 2.5.

2.3.4 Effect of treatment on pH, Al, and Fe content of the water solution throughout rice cultivation

The effects of treatments on the pH of water and Al and Fe content in water during the first and second seasons are shown in Figure 2.7. During the first season, the water samples were analyzed every week from 14 DAS until 119 DAS, whereas during the second season, the water samples were analyzed up to 77 DAS due to dry conditions. The pH of water ranged from 3.43 to 5.96 (first season) and from 3.46 to 7.13 (second season). The pH values of water for soil treated with GML and hydrated lime were higher compared to the control and soil treated with liquid lime throughout the first season. During the second season, the pH of water increased proportionally with rice growth from 28 DAS until 64 DAS for all treatments. Aluminium (Al) content in water for the first season was higher than during the second season, with the value ranging from 0.06 to 39.85 mg L⁻¹ and from 0.15 to 4.12 mg L⁻¹, respectively. During the first season, the Al content was < 2 mg L⁻¹ from 49 DAS onwards until the harvest. Water samples from soil treated with liquid lime contained a higher amount of Al compared to soil treated with GML, hydrated lime, and untreated soil. The iron content values were > 1 mg L⁻¹ throughout rice cultivation for both season, except during the first season at 21 DAS with the highest value of 87.53 mg L⁻¹ (soil treated with liquid lime).

Table 2.5**Effect of treatments on selected soil chemical properties after the harvests of the first and second seasons**

Season	Treatments	Exch-Al (cmol _c kg ⁻¹)	Exch Ca (cmol _c kg ⁻¹)	Exch Mg (cmol _c kg ⁻¹)	CEC (cmol _c kg ⁻¹)	Fe (mg kg ⁻¹)	P (mg kg ⁻¹)	C (%)	N (%)
1 st season	Control	7.27 ^a	0.51 ^{abc}	2.81 ^b	15.57 ^{ab}	333.32 ^a	11.90 ^a	2.85 ^a	0.28 ^a
	4 t ha ⁻¹ GML	8.35 ^a	0.70 ^{ab}	3.39 ^a	19.07 ^a	309.52 ^a	12.48 ^a	2.92 ^a	0.35 ^a
	2 t ha ⁻¹ HL	7.28 ^a	0.77 ^a	2.94 ^b	14.03 ^b	281.97 ^a	13.32 ^a	3.05 ^a	0.33 ^a
	20 L ha ⁻¹ LL	8.67 ^a	0.37 ^{bc}	2.96 ^b	14.41 ^b	264.45 ^a	12.17 ^a	2.42 ^a	0.30 ^a
	20 L ha ⁻¹ LL (2S)	8.72 ^a	0.33 ^c	3.07 ^b	15.29 ^{ab}	198.52 ^a	12.76 ^a	2.67 ^a	0.35 ^a
	2 t ha ⁻¹ HL (no F)	7.22 ^a	n.a	n.a	n.a	295.57 ^a	12.57 ^a	3.52 ^a	0.37 ^a
2 nd season	Control	6.73 ^a	0.60 ^b	3.01 ^b	13.9 ^{ab}	358.36 ^a	11.47 ^a	2.74 ^a	0.32 ^a
	4 t ha ⁻¹ GML	6.43 ^a	0.98 ^a	3.99 ^a	15.31 ^a	371.96 ^a	10.72 ^a	2.95 ^a	0.32 ^a
	2 t ha ⁻¹ HL	6.14 ^a	0.95 ^a	3.27 ^b	13.30 ^b	365.93 ^a	11.79 ^a	2.74 ^a	0.27 ^a
	20 L ha ⁻¹ LL	6.87 ^a	0.49 ^b	3.15 ^b	13.66 ^{ab}	335.18 ^a	11.19 ^a	2.39 ^a	0.24 ^a
	20 L ha ⁻¹ LL (2S)	6.84 ^a	0.45 ^b	3.07 ^b	14.29 ^{ab}	316.50 ^a	13.02 ^a	2.20 ^a	0.24 ^a
	2 t ha ⁻¹ HL (no F)	7.50 ^a	n.a	n.a	n.a	421.66 ^a	12.72 ^a	3.20 ^a	0.27 ^a

Means marked with the same letter for each season were not significantly different at $p < 0.05$ (Tukey's test)

*n.a: data not available

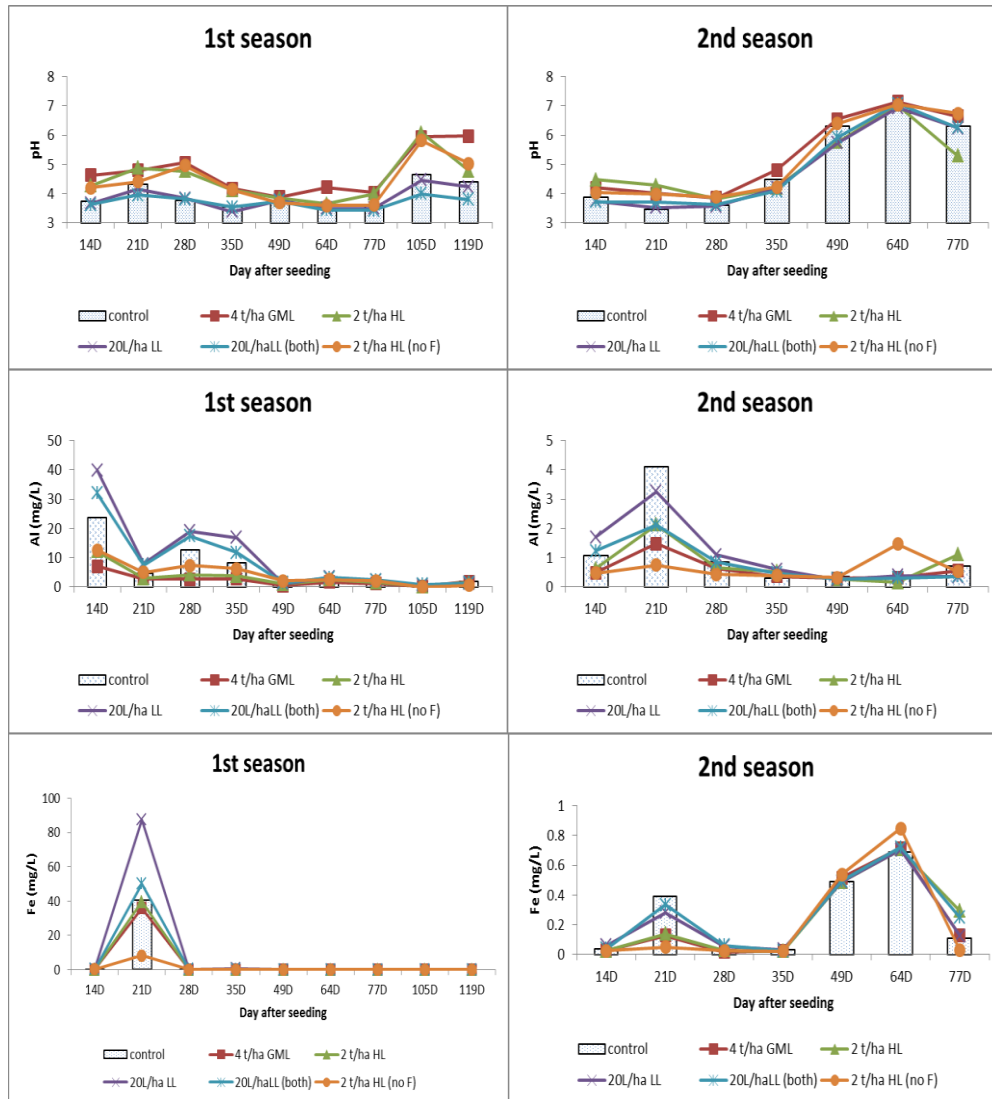


Figure 2.7 Effect of treatments on pH, Al, and Fe of water solution during the first and second seasons throughout rice cultivation.

2.3.5 Calcium (Ca) and Aluminum(Al) content of rice plants

Calcium and aluminum contents in the aboveground parts and root at 75 DAS for both seasons are shown in Figure 2.8. The calcium content in the root was lower than in the aboveground parts of rice plants. A significant effect was observed for Ca content between seasons in the aboveground parts and roots. No significant effects of Ca among the treatments during the second season in aboveground parts and roots were observed. Soil treated with 4 t ha⁻¹ GML showed a similar effect with 2 t ha⁻¹ hydrated lime without fertilizer, and these treatments were significantly higher than in soil treated with liquid lime and in untreated soil during the first season. The calcium content in roots ranged from 0.0003% to 0.0019% and from 0.0020% to 0.0040% during the first and second seasons, respectively. Calcium content in the root increased by 33.33% to 90% during the second season.

Aluminum content in the root was higher than in the aboveground parts. No significant effect on Al content among treatments was observed in aboveground parts during the second season. Soil treated with 4 t ha⁻¹ GML was significantly higher in Al content compared to untreated soil during the first season. In addition, no significant effect was observed on Al content in roots among treatments for both seasons.

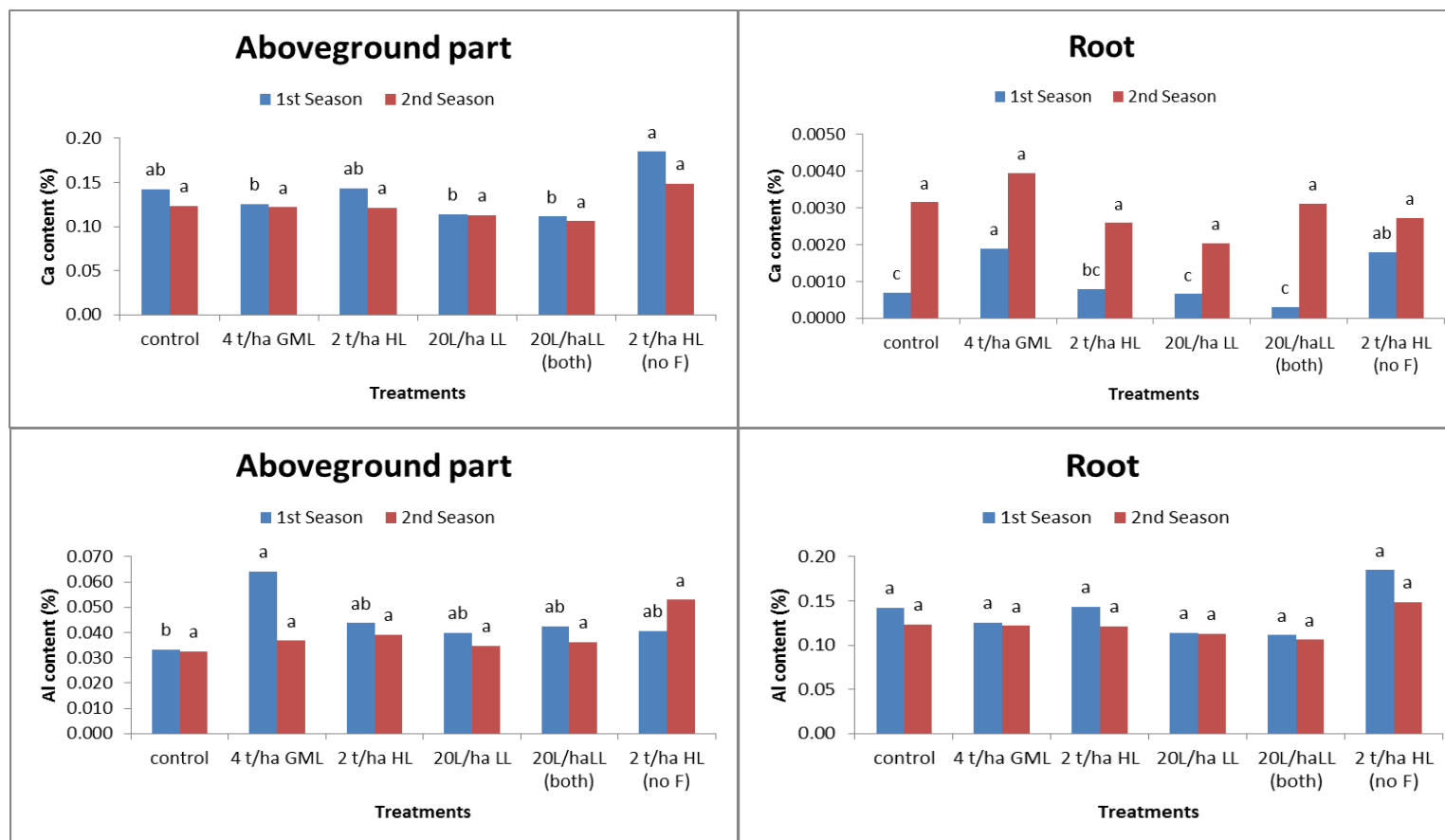


Figure 2.8 Calcium and aluminum content in the aboveground parts and roots at 75 days after sowing (DAS). Means marked with the same letter for each season were not significantly different at $p < 0.05$ (Tukey's test)

2.4 Discussion

2.4.1 Ameliorative effect

The soil investigated was low in pH and high in exchangeable Al (Table 2.1). Soil pH throughout the soil profile was < 3.5 . Exchangeable Al in the soil was very high throughout the soil depth. The topsoil (0–15 cm depth) comprises the zone where development of rice roots occurs. The pH values and exchangeable Al of the topsoil were 2.63 and $6.70 \text{ cmol}_c \text{ kg}^{-1}$, respectively. The pH values were lower than the critical level for rice production, whereas exchangeable Al exceeded the critical level for rice production of $1\text{--}2 \text{ mg kg}^{-1}$ as suggested by Dobermann and Fairhurst (2000). The pH and concentration of Al in the water at the soil pit was 3.70 and $878 \text{ }\mu\text{M}$, respectively. The concentration of Al far exceeded the critical toxic level of $74 \text{ }\mu\text{M}$ for rice growth (Dent, 1986). The favorable pH for optimal rice (MR 219) root growth is 6 (Alia et al., 2015). However, to raise the pH up to this level is costly, and many ordinary farmers may not be able to afford the measures required. Aluminium toxicity can occur in soil when $\text{pH} < 3.5$ (van Breemen and Pons, 1978). A study conducted in Japan showed that the growth of an Al-tolerant rice variety began to be inhibited when the Al^{3+} ion concentration exceeded $900 \text{ }\mu\text{M}$ (Cate and Sukhai, 1964). This value is close to the aluminium concentration observed in the current study at $878 \text{ }\mu\text{M}$; thus, rice growth in the current study area can be inhibited by Al. However, the rice plants grew well and provided a reasonable yield. Shamshuddin et al. (2013) stated that Al^{3+} is attracted to the negatively-charged cell walls of rice roots, thereby triggering the rice roots to secrete citric, oxalic, and malic acids. These acids in turn chelate the Al^{3+} , rendering it inactive. This defense mechanism allows rice plants to reduce the effects of Al^{3+} toxicity.

In the present experiment, a total of three liming materials were studied, namely ground magnesium lime (GML), hydrated lime, and liquid lime. The rate of liming materials studied were based on the farming practice in Malaysia, as shown in Table 2.2. All the liming materials used are available locally. Normally, farmers at the study area apply 2 t ha^{-1} of hydrated lime during the dry season (approximately March to April), because it is easier for machinery to enter the plot for lime application during this period. The farmers select hydrated lime because it provides rapid effects on their rice field upon application. From this experiment, the soil pH for soil treated with 2 t ha^{-1} hydrated lime (T3) showed the highest soil pH value of 3.36 compared to other treatments during the first season

(Figure 2.6). However, the soil pH decreased by 6.84% to a value of 3.13 during the second season. This indicated that the effect of hydrated lime on soil was temporary.

Based on the farmers practice and the improvement in soil pH by liming, lime application appears to be a viable alternative to ameliorate acidic soils for rice cultivation. From the present study, soil treated with 4 t ha⁻¹ GML provided the highest rice yield for both seasons with 3.71 t ha⁻¹ and 4.34 t ha⁻¹ during the first and second seasons, respectively (Table 2.4). Besides the increased rice yield, application of 4 t ha⁻¹ GML also significantly increased 1,000 grain weight compared to the control and soil treated with liquid lime (Table 2.4). Even though there was no significant effect of treatments on spikelet panicle⁻¹ and tillers number, soil treated with 4 t ha⁻¹ GML produced the highest spikelet and panicle and tiller numbers of 132 and 228 m⁻², respectively. This finding is further supported by Ting et al (1993), who noted that application of 2 t ha⁻¹ GML annually increased the rice yield to 4.5 t ha⁻¹, which is higher than the national average rice yield of 3.8 t ha⁻¹. The rice yields achieved in the present study for all treatments were higher than the yields achieved through normal farming practices (± 2 t ha⁻¹).

Adding GML show a positive effect as it significantly increased exchangeable Mg compared to other treatments, with values achieved during the first and second seasons of 3.39 and 3.99 cmol_c kg⁻¹. This value was above the critical value of 1 cmol_c kg⁻¹ as suggested by Dobermann and Fairhust (2000). In addition, GML significantly increased exchangeable Ca for both seasons. However, exchangeable Ca was below the require level of 2 cmol_c kg⁻¹ (Palhares de Melo et al., 2001). A higher amount of Ca in the soil results in rice plants that are able to assimilate higher amounts of Ca as shown in Figure 2.8. The positive effects shown by GML occur according to the following reactions:



The GML dissolved readily on application to the acidic soil, releasing Ca and Mg (Equation 2), and these macronutrients could be assimilated by the growing rice plants. Subsequently, hydrolysis of CO_3^{2-} (Equation 3) would produce hydroxyls that neutralized Al by forming inert Al-hydroxides (Equation 4). In addition, soil to which GML was applied showed significantly increased cation exchange capacity (CEC) compared to soil which received liquid lime (Table 2.5).

The ameliorative effects of liming materials were improved during the second season (Figure 2.9 and 2.10). The relationships between soil pH and relative rice yield during the first and second seasons are shown in Figure 2.9, as this indicates that the relative rice yield positively correlated with soil pH. The regression line for the second season shifted to a higher level, showing that the relative rice yield had increased after the first season, even though the soil pH ranged between 2.9 to 3.4 (high acidity) for both seasons. Despite this fact, there was only a 10% drop in relative rice yield corresponding to a change in soil pH of 3.38 and 3.17 for first season and second seasons, respectively.

The relationship between exchangeable Al and relative rice yield is shown in Figure 2.10. After the second season, the regression line was shifted to the left. This indicated that the Al toxicity had been reduced (ameliorative effect) after the second season. A 10% drop in relative rice yield corresponding to exchangeable Al of 6.13 and 6.67 $\text{cmol}_c \text{ kg}^{-1}$ for first season and second seasons, respectively was evident. However, no significant difference was observed among treatments for exchangeable Al (Table 2.5).

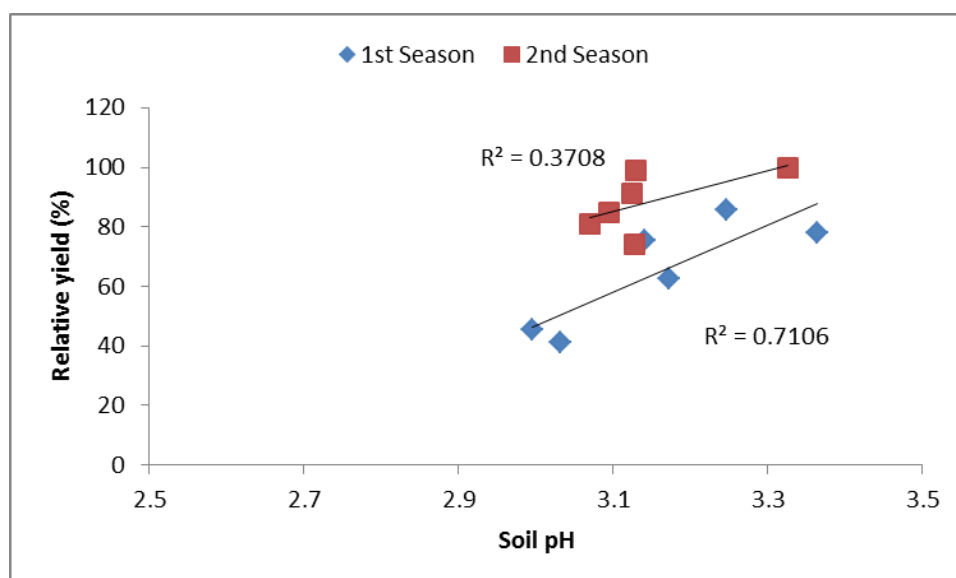


Figure 2.9 Relationships between soil pH and relative yield during first and second seasons

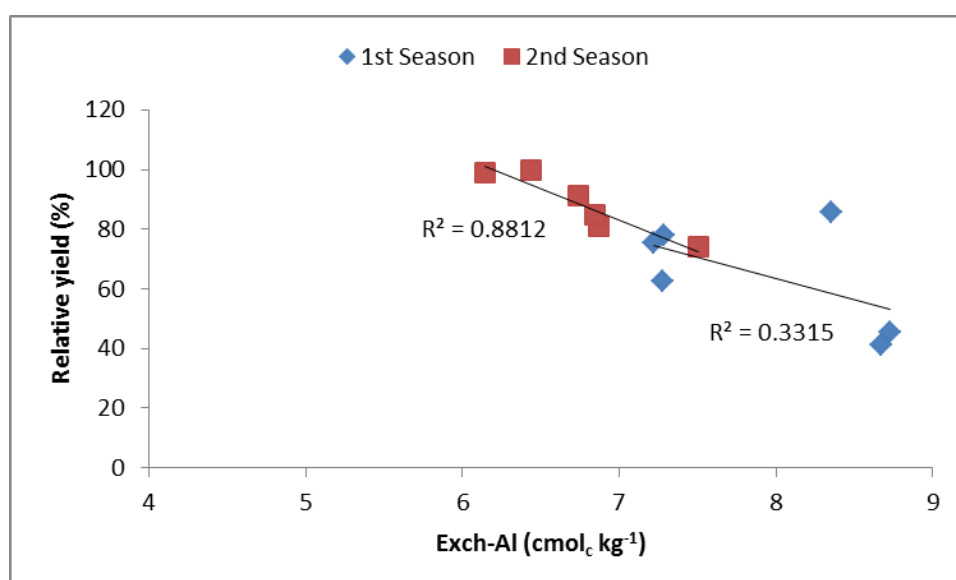


Figure 2.10 Relationships between exchangeable Al and relative yield during the first and second seasons

Soil treated with liquid lime produced a rice yield of $< 2 \text{ t ha}^{-1}$ during the first season, and a consistently low soil pH of 3 was noted. Liquid lime is applied as a solution, and lime is suspected to be quickly leached through the soil column. In addition, the particle size of liquid lime ($1.5\text{--}5 \mu\text{M}$) is far smaller than GML (20–200 mesh size) and hydrated lime (± 200 mesh size), which are in a powdered form. Smaller size particles are often subjected to faster losses through leaching than larger size particles.

Growing rice in an area with low pH and high Al concentration would inhibit the elongation of plant roots (Horst et al., 2009; Alia et al., 2014). The disruption of the root cap forming processes and a decline in cell division and deposition of lignin would occur (Susan et al., 2007). As a result, nutrient uptake is curtailed, and multiple nutrient deficiencies occur (Godbold et al., 1988; Ridolfi and Garrec, 2000). These assertions have been confirmed by the present study, which showed that the concentration of Ca in roots was significantly higher with 4 t ha^{-1} GML application compared to control, 2 t ha^{-1} hydrated lime application, and 20 L ha^{-1} liquid lime application (Figure 2.8). As an improved ameliorative effect was shown during the second season, Ca content in the rice root increased by 33.33% to 90.20% during the second season for all treatments. However, no significant difference was observed among the treatments.

Besides soil acidity and Al toxicity, farmers in the area face the additional challenge of drought (Figure 2.4a). Bouman and Tuoang (2001) stated that lowland rice is extremely sensitive to water shortages and drought problems when soil water contents drop below saturation, and this will reduce leaf area expansion and result in closure of stomata, leaf rolling, deeper root growth, enhanced leaf senescence, reduced plant height, delayed flowering, and reduced number of tillers, panicle, spikelet, and grain weight. In the current study, the paddy field was dry when the seeds were sown during the first season. There was no proper water irrigation and drainage system in place, resulting in dependence solely on rain water, which falls erratically throughout the growing season; hence, crop watering was insufficient. As a result, the sown seeds did not germinate well, and the seedlings suffered because their roots were unable to tap the underground water. Therefore, water was pumped in from the nearest canal to germinate the seeds (Figure 2.4b). This had affected the subsequent growth of rice seedlings and hence, the eventual rice yield. However, treatments with GML and hydrated lime raised the pH of water throughout rice planting, with pH ranging from 4 to 6, as shown in Figure 2.7.

An ameliorative effect was shown during the subsequent season (second season) as water pH was increased drastically between 28 to 64 days after seeding for all treatments. In addition, Al and Fe of water were also alleviated from 4.12 to 0.3 mg L⁻¹ and from 0.84 to 0.02 mg L⁻¹, respectively.

2.4.2 Cost-benefit analysis of liming materials

Based on the normal farming practice, the rice yields are often $\pm 2 \text{ t ha}^{-1}$ in the studied acid sulfate soil area, and this is far below the national average of 3.8 t ha^{-1} . From the present study, soil amendment with liming materials (GML, hydrated lime, and liquid lime) are noted to increase rice yield at an average of 30%. Thus, to increase the income of farmers and reduce production costs, a cost-benefit analysis is presented in Table 2.6. Fertilizer and pesticides used by farmers are subsidized by the Malaysian government to promote agricultural sustainability in the rural areas. Therefore, the cost for liming materials and labor cost to apply liming materials were taken into account. The net profit was calculated based on rice yield for a year per hectare. Rice yield had increased by 14% to 50% during the second season due to treatments applied along with fertilizers. The rice yield for soil treated with 2 t ha^{-1} hydrated lime without fertilizer recorded a minimal decrease of 1.55%. Application with 4 t ha^{-1} GML recorded the highest rice yield for both seasons, with yields of $3.71 \text{ t ha}^{-1} \text{ season}^{-1}$ and $4.34 \text{ t ha}^{-1} \text{ season}^{-1}$ for the first and second seasons, respectively. GML application produced significantly improved yield; however, it comes with a cost. The cost to treat the soil with 4 t ha^{-1} GML was USD 380, providing the highest rice yield with $8.05 \text{ t ha}^{-1} \text{ year}^{-1}$ compared to other treatments. The selling price of rice is USD 315 t^{-1} , and for $8.05 \text{ t ha}^{-1} \text{ year}^{-1}$, this roughly provides a profit of USD 2,156 per hectare per year.

Table 2.6

Cost-benefit analysis of liming materials used. Means marked with the same letter for each season were not significantly different at $p < 0.05$ (Tukey's test)

		Control	4 t ha ⁻¹ ground magnesium limestone	2 t ha ⁻¹ hydrated lime	20 L ha ⁻¹ liquid lime (applied only 1 st season)	20 L ha ⁻¹ liquid lime (applied 1 st and 2 nd seasons)	2 t ha ⁻¹ hydrated lime (without fertilizer)
Rice yield (t ha ⁻¹)	Season 1 (a)	2.71 ^{ab}	3.71 ^a	3.38 ^{ab}	1.79 ^b	1.97 ^b	3.26 ^{ab}
	Season 2 (b)	3.95 ^a	4.34 ^a	4.29 ^a	3.52 ^a	3.68 ^a	3.21 ^a
	Yield increment (%)	+31.39	+14.52	+21.21	+49.15	+46.46	-1.55
	Total yield (a+b)	6.66	8.05	7.67	5.31	5.65	6.47
Cost for liming	Price	-	USD 50 t ⁻¹ = USD 200	USD 140 t ⁻¹ = USD 280	USD 97 20L ⁻¹ = USD 97	USD 97 20L ⁻¹ = USD 194	USD 140 t ⁻¹ = USD 280
	Labour	-	USD 45 t ⁻¹ = USD 180	USD 45 t ⁻¹ =USD 90	USD 16 ha ⁻¹ = USD 16	USD 16 ha ⁻¹ =USD 32	USD 45 t ⁻¹ =USD 90
	^d Total		USD 380	USD 370	USD 113	USD 226	USD 370
Price of rice (USD 315/ t)	^c Total price for yield	USD 2098	USD 2536	USD 2416	USD 1673	USD 1780	USD 2038
Profit	c-d	USD 2098	USD 2156	USD 2046	USD 1560	USD 1554	USD 1668

2.4.3 Treatment without fertilizer

No significant effects were observed on rice yield and rice yield components between plots treated with 2 t ha^{-1} hydrated lime with fertilizer (T3), and without fertilizer application (T6) for both seasons. However, plots treated with 2 t ha^{-1} hydrated lime with fertilizer (T3) showed a yield increment during the following season (second season) of 21.21%, whereas plots treated with 2 t ha^{-1} hydrated lime without fertilizer showed a small decrease in rice yield of 1.55%. The total yields obtained for T3 and T6 for a year were $7.67 \text{ t ha}^{-1} \text{ year}^{-1}$ and $6.47 \text{ t ha}^{-1} \text{ year}^{-1}$, respectively. The differences between the two season was 1.2 t ha^{-1} of rice yield. From the result, it is evident that the application of fertilizer is not necessary for at least one season (T6) at the respective area. Therefore, farmers could reduce costs by reducing fertilizer application.

2.5 Conclusions

Application of GML and hydrated lime increased rice yields for both seasons, in contrast to liquid lime application which achieved no increase in rice yield on acidic sulfate soil as compared to the control for both seasons. However, ground magnesium limestone (GML) was a suitable liming material at the studied area (under acid sulfate soil conditions). Application of $4 \text{ t ha}^{-1} \text{ year}^{-1}$ increased rice yield by 31.39%. Thus, the highest recorded rice yield was $8.05 \text{ t ha}^{-1} \text{ year}^{-1}$ with a calculated profit of USD 2,156 compared to other treatments.

Chapter 3 Improve the fertility of acidic sulfate soil with application of ground magnesium limestone (GML)

3.1 Introduction

Merbuk (Kedah) is located in northwest of Peninsular Malaysia. Under agriculture system, soils at these areas are cultivated with rice. Average rice yield in these areas per season is often less than 2 t ha^{-1} , which is lower than national average rice yield of 3.8 t ha^{-1} . Reduction in yield at such a rate is mainly due to the soil acidity. As such, soils in Malaysia are highly weathered soils, and many part of the region are classified as either Ultisol and/or Oxisol. These are soils marked with high acidity and high Al content. Soils at Merbuk are acidic soil with $\text{pH} < 3.5$ and high in aluminum (Al) content in soil.

Liming is a common approach to alleviate soil acidity and improve soil fertility for agriculture purpose in Malaysia. A suggested lime rate used is between 1.5 to 5 t ha^{-1} of ground magnesium limestone (GML) for rice cultivation based on soil pH with higher soil pH require higher amount of lime. This suggestion was brought forward by the Department of Agriculture Malaysia, Ministry of Agriculture, Malaysia (2006) in a book entitled *Manual Tanaman Padi: Teknik Tabur Terus*. In the past, several studies have been conducted to improve acidic soil using GML for agriculture purposes in Malaysia with mixed success. Besides increase soil pH, GML also supply calcium (Ca) and magnesium (Mg) to soil and plant uptake. This is due to the main constituent in GML are 40% CaO and 15% MgO. Based on Shazana et al. (2013), application of 4 t ha^{-1} GML were able to produce rice yield up to 4.21 t ha^{-1} in Kelantan area. GML potential has also been highlighted by Ting et al. (1993), that 2 t ha^{-1} annually can produce rice yield of $4.5 \text{ t ha}^{-1} \text{ season}^{-1}$. Besides that, GML in-combination with organic matter was able to produce rice yield of 7.5 t ha^{-1} (Suswanto et al., 2007). Furthermore, the beneficial effects of liming the soil with GML at 4 t ha^{-1} have been observed for about eight years by Shamshuddin et al. (1998).

GML was selected and used because it can be easily obtained and available locally. However, the price of GML keeps on increasing. From the farmers' perspective, the more they apply onto their soil; it would be better for their soil hence increase their yield. However, it would increase their cost of input and labor cost.

In previous chapter (Chapter 2), addition of 4 t ha⁻¹ GML was suitable rate as soil amendments to increase the rice yield on acidic soil at Merbuk (Kedah). Therefore, the main objective of this study was to evaluate the effect of GML and to assess the possibility of reducing current application rate of 4 t ha⁻¹ commonly used by farmers to improve the fertility of acidic sulfate soil in Malaysia. The results from this study would be useful for reclamation of degraded and abandoned paddy field in Malaysia at large.

3.2 Materials and methods

3.2.1 Soil used for the experiment

Soil used in the experiment were obtained from Merbuk rice field located in northwest of Peninsular Malaysia (Figure 2.1). Merbuk area is covered with paddy field, with low rice yield (average less than 2 t ha⁻¹ season⁻¹). In addition, these rice cultivation areas are under rain-fed condition.

Studies related to Chapters 3, 4 and 5 were conducted at the north of Peninsular Malaysia and a field experimental plot was established at Location 2 (Figure 2.2). Unfortunately, the rice crop did not grow. Rice seeds were sown three times in total (Figure 3.1–Figure 3.5); however, with no success. During the first sowing (Figure 3.1), the rice seed only lasted between 7–14 days. During the second sowing, rice seeds between 14–21 days; however, *Purun* (a local weed) simultaneously grew within the rice plot. Rice seeds were unable to compete with *Purun* and were, thus, unable to grow further (Figure 3.2 and 3.3). During the third sowing, the rice seeds only lasted approximately 7–14 days (Figure 3.4), and water dried out, leaving cracked topsoil, and *Purun* further outgrew the rice seeds (Figure 3.5) in the experimental plots. The presence of *Purun* is an indicator of high soil acidity. Local farmers at the respective area (Bujang) would at best only be able to cultivate a rice crop once per year. Therefore, the soils were collected from Location 2 (Figure 2.2) and transported back to Field 2 (3° 00'31.63" N 101° 42'18.87" E) in Universiti Putra Malaysia (UPM) under rain shelter conditions. A composite soil sample of approximately 2500 g was taken from 0-15 cm depth using an auger. The sample was taken within a 0.5 ha region of the rice cropped area. Afterward, the soil was crushed, passed through a 2 mm sieve, and mixed thoroughly prior to incubation.

3.2.2 Treatments and experimental design

Treatments used were (i) control (no lime); (ii) 2 t ha⁻¹ GML; (iii) 4 t ha⁻¹ GML and (iv) 6 t ha⁻¹ GML henceforth will be referred as G0, G2, G4 and G6. Lime was incorporated with 500g soil prior to submerge the soil with water. Soil and water were sampled at 30, 60, 90 and 120 days of incubation. Experimental design used in this experiment was Completely Randomized Design (CRD) with three replications.



Figure 3.1 Plot preparation and first sowing of rice seed. Photo taken on 12th April 2014



Figure 3.2 Second sowing of rice seed. First week of rice plant growth (left). Rice seed have to compete with *Purun* (local weed) plant (right). Photo taken on 9th May 2014



Figure 3.3 Second times sowing of rice seed. Second week of rice growth (left). Stunted with no root growth (right). Photo taken on 23rd May 2014



Figure 3.4 Third sowing of rice seed. First week of rice growth (left). Rice seeds unable to grow. Photo taken on 2nd June 2014



Figure 3.5 The experimental plot land was too dry, and *Purun* (local weed) was growing as an indicator of the soil being too acidic. Photo taken on 23rd June 2014

3.2.3 Soil analyses

Soil samples were air-dried, ground, and passed through a 2 mm sieve prior to chemical analyses. Soil pH was determined in water at a ratio of 1:2.5 (soil: distilled water) using a glass electrode pH meter (Metrohm 827 pH meter). Total C, N, and S were determined using CNS Analyzer Leco RC-412C Leco Corporation, St. Joseph MI. Cation exchange capacity (CEC) was determined using 1 M NH_4OAc at pH 7 (Chapman, 1965). Exchangeable Ca, Mg, K, and Na were determined using 1 N NH_4Cl (Ross and Ketterings, 1995; Shamshuddin, 2006). The procedure was as follows; Two (2) g of air-dried soil was placed in a 50 mL centrifuge tube and 20 mL 1 N NH_4Cl was added. The sample was shaken for 2 h on an end-to-end shaker at 150 rpm, followed by centrifugation at 2500 rpm for 15 min. The extract was passed through a filter paper Whatman No. 42 into a 50 mL plastic vial. The exchangeable Ca, Mg, K, and Na in the extract were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA). Exchangeable Al was determined by extracting 5 g of soil with 50 mL of 1 M KCl. The mixture was then shaken for 30 min and filtered, and the extracted Al was analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA). Extractable Fe, Cu, Zn, and Mn were extracted using extracting agent (0.05 N

HCl and 0.025 N H₂SO₄). The procedure was as follows; Five (5) g of air-dried soil was shaken with 25 mL of extracting agent for 15 min. The extract was passed through a filter paper Whatman No. 42 and used to determine Fe, Cu, Zn, and Mn by Atomic Absorption Spectrometry (AAS Perkin Elmer, model 1100B). Additionally, 0.01 M CaCl₂ was used to extract plant-available Si from the soil. For this, 2 g of soil was shaken for 16 h with 20 mL CaCl₂ extractant in a 50 mL centrifuge tube on an end-to-end shaker. The sample was centrifuged at 2000 rpm for 10 min before the supernatant was filtered through a filter paper Whatman No. 42 and analyzed for Si (Narayanaswamy and Prakash, 2009)) using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA).

3.2.4 Water analyses

Water sample of flooded water from each pot was collected together with soil samples. Water samples were filtered using filter paper Whatman No. 42. The pH of water was determined using pH meter (Metrohm 827 pH meter). Aluminum (Al), Calcium (Ca), Magnesium (Mg), Iron (Fe) and Silicon (Si) were measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA, while Phosphorus (P) and Potassium (K) were measured using an auto-analyser (Quick Chem 8000 Series FIA+System; Lachat Instruments, Loveland, USA).

3.2.5 Statistical analyses

Statistical analyses for means comparison were done using Tukey's test by SAS version 9.2 (SAS, Institute, Inc., Cary, NC). Diagrams in this paper were drawn using the Excel program with Microsoft® 2010.

3.3 Results

Changes of selected chemical soil characteristics in acidic sulfate soil amended with different rate of GML (0, 2, 4 and 6 t ha⁻¹) are shown in Figure 3.6 until 3.13. The soil chemical characteristics are soil pH, exchangeable Al, exchangeable Ca, exchangeable Mg, exchangeable K, Fe content, available P and Si content. The effect of GML applied on each of soil chemical properties was compared for each incubation days. Each days of incubation represent rice phase of vegetative, reproductive, flowering and maturity at 30, 60, 90 and 120 days of incubation, respectively. The means marked with the same letter for each days of incubation are not significantly different at $p < 0.05$ (Tukey's Test).

3.3.1 Initial soil chemical characteristics

Selected chemical properties of soil used for this experiment are shown in Table 3.1. The topsoil (0-15 cm depth) is the zone where the development of rice roots occurs. The pH for the topsoil was low at pH 2.89. The soil pH throughout the soil depth was lower than pH 3.5. Exchangeable Al increased with soil depth, and the exchangeable Al at the topsoil was above the critical value of 2 cmol_c kg⁻¹ as stated by Hiradate et al. (2007). According to van Breemen and Pons (1978), aluminum toxicity could occur when soil pH is at pH < 3.5. Exchangeable Ca and Mg for topsoil were 0.85 and 2.01 cmol_c kg⁻¹ below critical level of 2 cmol_c kg⁻¹ as stated by Palhares (2000) and within the sufficiency level of 1 cmol_c kg⁻¹ as highlighted by Dobermann and Fairhurst (2000), respectively. Exchangeable cations except for exchangeable K increased with soil depth. Total carbon, nitrogen and sulphur for topsoil were 2.34, 0.14 and 0.10 %, respectively. Silicon (Si) content in the soil ranged from 25.80 to 38.40 mg kg⁻¹ throughout the soil depth. Silicon value for the topsoil was below the critical level for crop production of 43 mg kg⁻¹ as highlighted by Narayanaswamy and Prakash (2009).

Table 3.1**Initial soil chemical characteristics of soils from Merbuk (Kedah)**

Depth	Soil	Exchangeable cation					CEC	ECEC	Extractable					Total			Al
(cm)	soil:water	K	Ca	Mg	Na	Al			Fe	Cu	Zn	Mn	Si	C	N	S	saturation
	1:2.5	-----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

3.3.2 Effect of GML on soil pH

Figure 3.6 shows the effect of GML application on soil pH for each days of incubation. The soil pH increased as the rate of GML increased. The soil pH for untreated soil was below than 4.

At 30 days of incubation, the pH values were ranged from 3.63 to 4.26 and no significant effect were observed among treatments.

At 60 days of incubation, the soil pH values were ranged from 3.71 to 4.49. Soil treated with 6 t ha⁻¹ GML was significantly increased the soil pH compared to other treatments. No significant effect was observed among 0, 2 and 4 t ha⁻¹ GML.

At 90 days of incubation, the soil pH was ranged from 3.41 to 4.08 and no significant effect was observed among treatments.

At 120 days of incubation, the soil pH was ranged from 3.65 to 4.42. Soil treated with 6 t ha⁻¹ GML was significantly increased soil pH compared to other treatments while no significant effect was observed between soil treated with 0, 2 and 4 t ha⁻¹ GML.

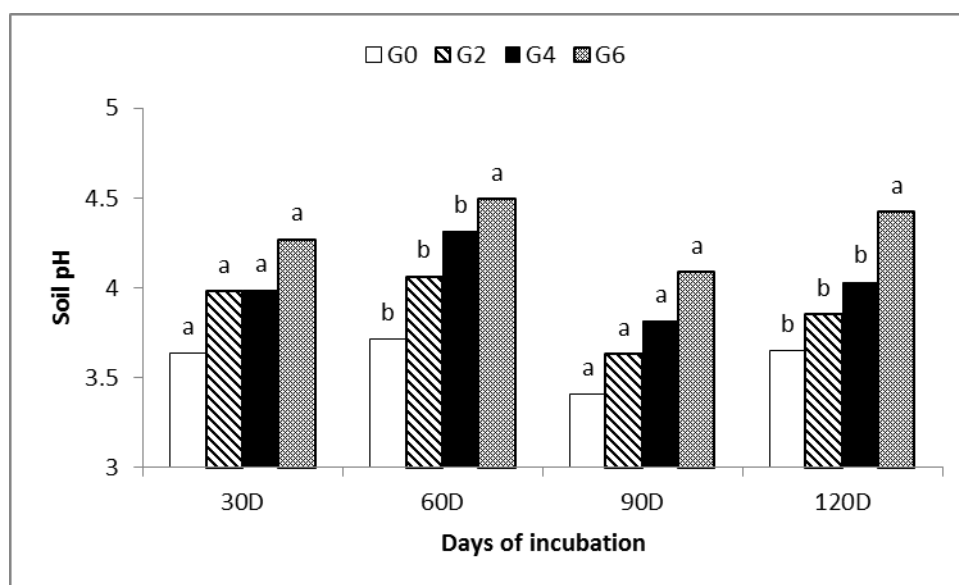


Figure 3.6 Changes of soil pH on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.3 Effect of GML on exchangeable aluminium (Al)

Figure 3.7 shows the effect of GML application on exchangeable Al. The exchangeable Al was reduced after addition of GML corresponding with the incubation period. Untreated soils were significantly higher compared to treated soil for entire days of incubation. Untreated soils were above the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$ at 30 and 60 days of incubation values of 3.34 and $2.77 \text{ cmol}_c \text{ kg}^{-1}$, respectively.

At 30 days of incubation soils treated with 2 and 4 t ha^{-1} GML was significantly reduced compared to untreated soils but no significant effect between these two treatments, while soils treated with 6 t ha^{-1} GML was significantly reduced the exchangeable Al compared to other treatments value of $0.65 \text{ cmol}_c \text{ kg}^{-1}$.

At 60 days of incubation, soils treated with 2 , 4 and 6 t ha^{-1} GML was significantly reduced the exchangeable Al compared to untreated soils with values of 1.62 , 0.78 and $0.36 \text{ cmol}_c \text{ kg}^{-1}$, while no significant effect were observed between soil treated with 4 and 6 t ha^{-1} GML.

At 90 and 120 days of incubation, exchangeable Al for all treatments was below the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$. However, soil treated with 2 , 4 and 6 t ha^{-1} GML were significantly reduced compared to untreated soil. No significant effect were observed between soil treated with 2 , 4 and 6 t ha^{-1} GML at 90 days of incubation while no significant effect were observed between 2 and 4 t ha^{-1} GML and between 4 and 6 t ha^{-1} GML at 120 days of incubation.

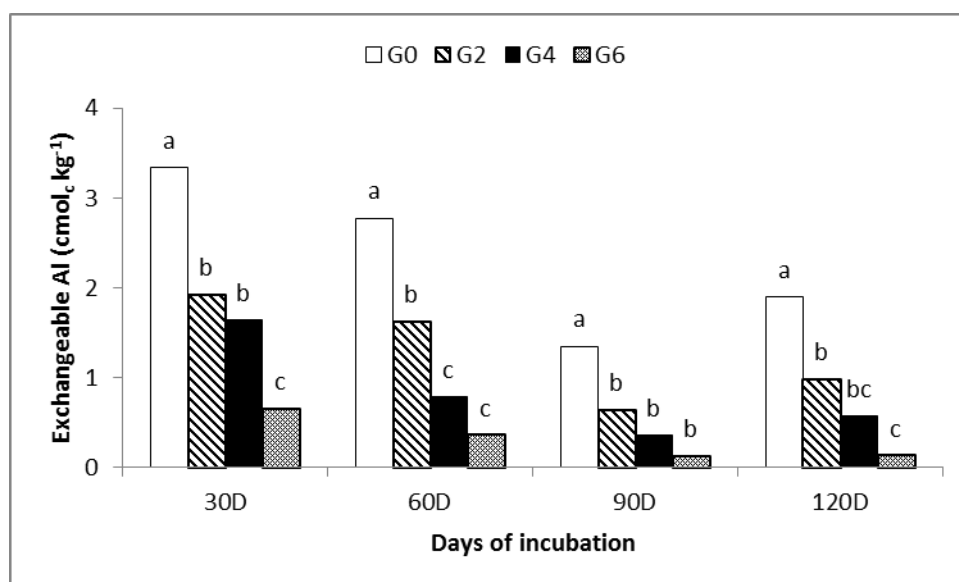


Figure 3.7 Changes of exchangeable Al on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.4 Effect of GML on exchangeable calcium (Ca)

Figure 3.8 shows the effect of GML on exchangeable calcium (Ca) at 30, 60, 90 and 120 days of incubation. Exchangeable Ca increased with increasing rate of GML. Soil treated with 6 t ha⁻¹ GML was gave the highest value compared to other treatments at 30, 60, 90 and 120 days of incubation with values of 5.07, 5.03, 2.91 and 6.24 cmol_c kg⁻¹, respectively.

At 30 days of incubation, soil treated with 2, 4 and 6 t ha⁻¹ GML were significantly increased the exchangeable Ca compared to untreated soils while no significant effect were observed between soil treated with 2 and 4 t ha⁻¹ GML with values of 3.73 and 4.12 cmol_c kg⁻¹.

At 60 days of incubation, soil treated with 2, 4 and 6 t ha⁻¹ GML were significantly increased the exchangeable Ca compared to untreated soil with values of 3.30, 4.15 and 5.03 cmol_c kg⁻¹, respectively.

At 90 days of incubation, soil treated with 6 t ha⁻¹ GML were significantly increased the exchangeable Ca compared to soil treated with 0 and 2 t ha⁻¹ GML. No significant effect was observed between soil treated with 0 and 2 t ha⁻¹ GML and between 4 and 6 t ha⁻¹ GML with values of 1.67, 1.82, 2.33 and 2.91 cmol_c kg⁻¹.

At 120 days of incubation, soil treated with 2, 4 and 6 t ha⁻¹ GML were significantly increased the exchangeable Ca compared to untreated soil with value of 3.94, 4.58 and 6.24 cmol_c kg⁻¹, respectively. No significant effect was observed between soil treated with 2 and 4 t ha⁻¹ GML.

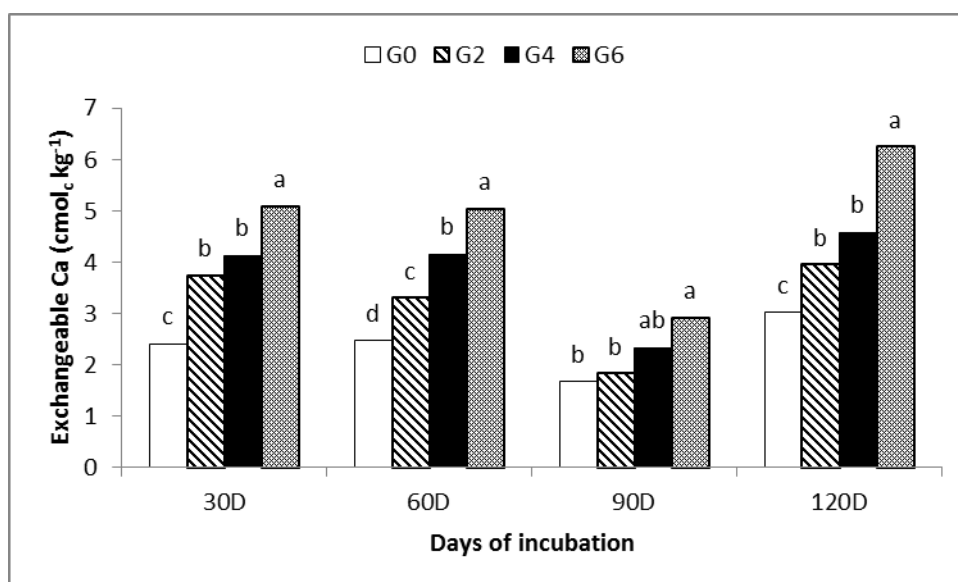


Figure 3.8 Changes of exchangeable Ca on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.5 Effect of GML on exchangeable magnesium (Mg)

Figure 3.9 shows the effect of GML on exchangeable magnesium (Mg) at 30, 60, 90 and 120 days of incubations. The exchangeable Mg was increased with increasing rate of GML for each days of incubation. Soil treated with 6 t ha⁻¹ GML gave the highest values of 4.84, 4.78, 2.35 and 5.19 cmol_c kg⁻¹ at 30, 60, 90 and 120 days of incubation, respectively.

At 30 days of incubation, soil treated with 2, 4 and 6 t ha⁻¹ GML were significantly increased the exchangeable Mg compared to untreated soil. No significant effect was observed between soil treated with 2 and 4 t ha⁻¹ GML values of 3.79 and 4.16 cmol_c kg⁻¹, respectively.

At 60 days of incubation, soil treated with 2, 4 and 6 t ha⁻¹ GML were significantly increased exchangeable Mg compared to untreated soil with values of 3.57, 4.23 and 4.78 cmol_c kg⁻¹.

At 90 days of incubation, no significant effect were observed among treatments with values of 1.79, 1.76, 2.03 and 2.35 cmol_c kg⁻¹ for 0, 2, 4 and 6 t ha⁻¹ GML, respectively. The exchangeable Mg was reduced by 43% to 52% from soil treated at 60 days of incubation.

At 120 days of incubation, soil treated with 4 and 6 t ha⁻¹ GML were significantly increased the exchangeable Mg compared to untreated soils while soil treated with 6 t ha⁻¹ GML was significantly increased the exchangeable Mg compared to other treatments. No significant effect was observed between soil treated with 2 and 4 t ha⁻¹ GML values of 3.65 and 4.10 cmol_c kg⁻¹, respectively.

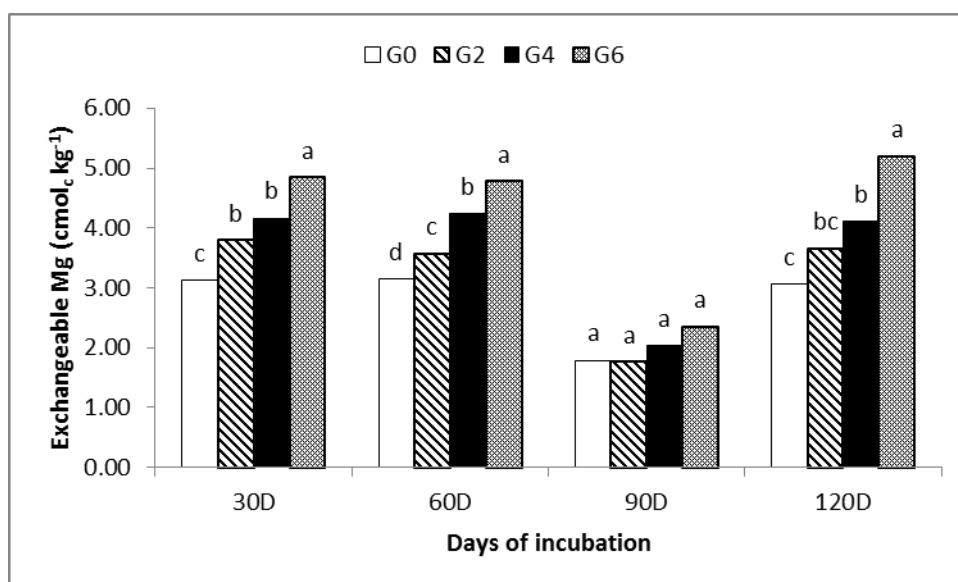


Figure 3.9 Changes of exchangeable Mg on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.6 Effect of GML on exchangeable potassium (K)

Figure 3.10 shows the effect of GML on exchangeable K at 30, 60, 90 and 120 days of incubation. No significant effect was observed among treatments at 30, 60, 90 and 120 days of incubation.

The exchangeable K was ranged from 0.47 to 0.55 and from 0.49 to 0.58 $\text{cmol}_c \text{kg}^{-1}$ at 30 and 60 days of incubation, respectively.

At 90 days of incubation, the exchangeable K was reduced by 46.55% to 65.38% from 60 days of incubation values of 0.31, 0.20, 0.18 and 0.19 for 0, 2, 4, and 6 t ha^{-1} GML, respectively.

At 120 days of incubation, the exchangeable K values were 0.52, 0.49, 0.47 and 0.52 $\text{cmol}_c \text{kg}^{-1}$ for 0, 2, 4 and 6 t ha^{-1} GML, respectively.

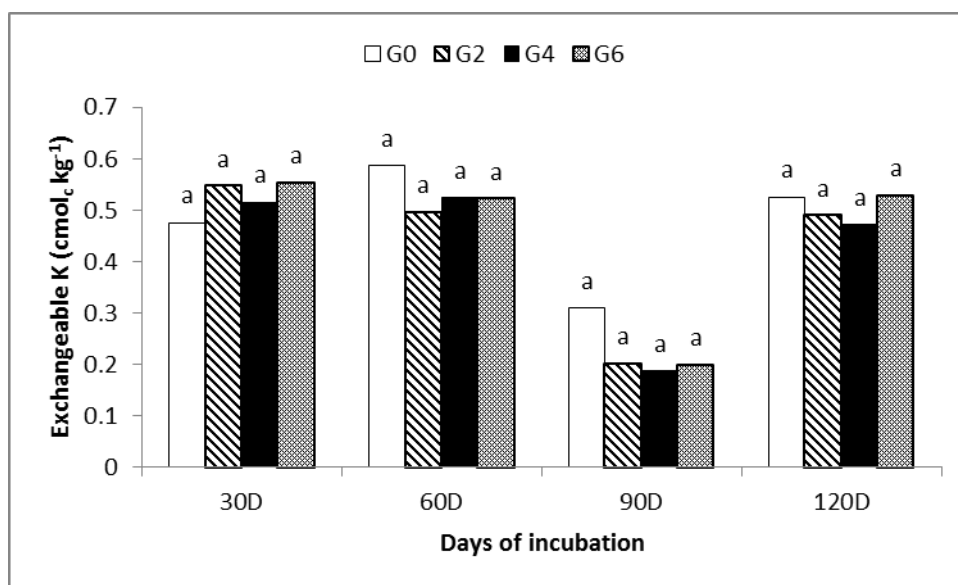


Figure 3.10 Changes of exchangeable K on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.7 Effect of GML on exchangeable iron (Fe)

Figure 3.11 shows the effect of GML on the exchangeable Fe at 30, 60, 90 and 120 days of incubation. The exchangeable Fe was reduced with increasing rate of GML at each days of incubation. The highest value recorded was $0.52 \text{ cmol}_c \text{ kg}^{-1}$ while the lowest value was $0.03 \text{ cmol}_c \text{ kg}^{-1}$.

At 30 days of incubation, soil treated with 2, 4 and 6 t ha^{-1} GML were significantly reduced the exchangeable Fe compared to untreated soils value of 0.21, 0.06 and $0.09 \text{ cmol}_c \text{ kg}^{-1}$, respectively. No significant effect was observed between soil treated with 4 and 6 t ha^{-1} GML.

At 60 days of incubation, soil treated with 2, 4 and 6 t ha^{-1} GML were significantly reduced the exchangeable Fe compared to untreated soil values of 0.19, 0.09 and $0.04 \text{ cmol}_c \text{ kg}^{-1}$, respectively while no significant effect was observed between soil treated with 4 and 6 t ha^{-1} GML.

At 90 days of incubation, soil treated with 4 and 6 t ha^{-1} GML were significantly reduced the exchangeable Fe compare to untreated soil and no significant effect was observed between these both treatments. No significant effect was observed between untreated soil and soil treated with 1 t ha^{-1} GML. The exchangeable Fe was reduced by 22.22% to 46.15% from 60 days of incubation with values of 0.21, 0.12, 0.07 and $0.03 \text{ cmol}_c \text{ kg}^{-1}$ for 0, 2, 4 and 6 t ha^{-1} GML, respectively.

At 120 days of incubation, soil treated with 2, 4 and 6 t ha^{-1} GML were significantly reduced the exchangeable Fe compared to untreated soil values of 0.23, 0.14 and $0.05 \text{ cmol}_c \text{ kg}^{-1}$, respectively. No significant effect was observed between these three treatments.

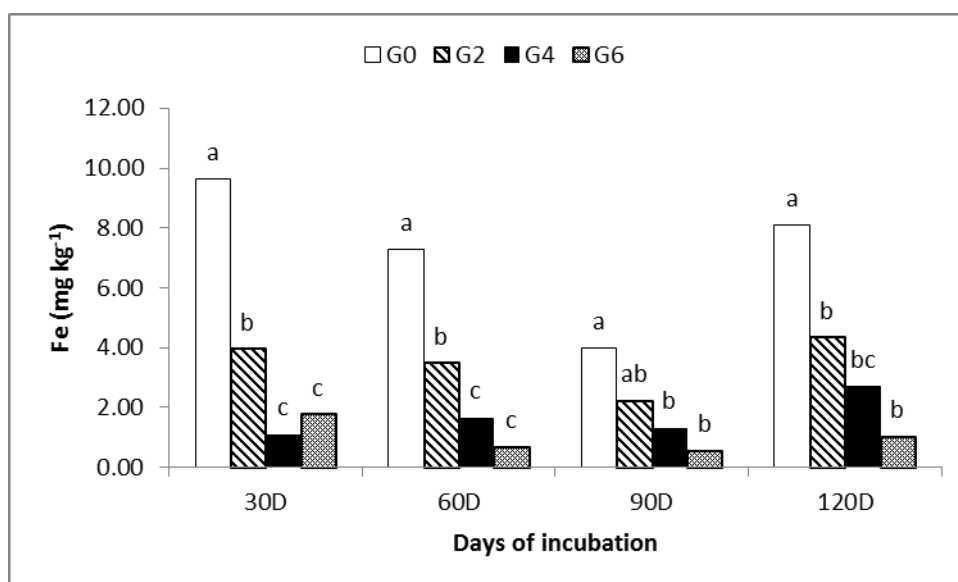


Figure 3.11 Changes of Fe on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.8 Effect of GML on available phosphorus (P)

Figure 3.12 shows the effect of GML on available P at 30, 60, 90 and 120 days of incubation. No significant effect was observed among treatments at 30, 60 and 90 days of incubation. The available P was ranged between 18.25 to 18.85 mg kg⁻¹ and 18.15 to 19.97 mg kg⁻¹ at 30 and 60 days of incubation, respectively.

At 90 days of incubation, the available P was reduced by 22.58% to 28.24% from 60 days of incubation with the values of 14.33, 13.93, 14.05 and 14.47 for 0, 2, 4 and 6 t ha⁻¹ GML.

At 120 days of incubation, the soil treated with 6 t ha⁻¹ GML, was significantly increased the available P compared to other treatments value of 16.75 mg kg⁻¹. No significant effect was observed between untreated soil, soil treated with 2 and 4 t ha⁻¹ GML.

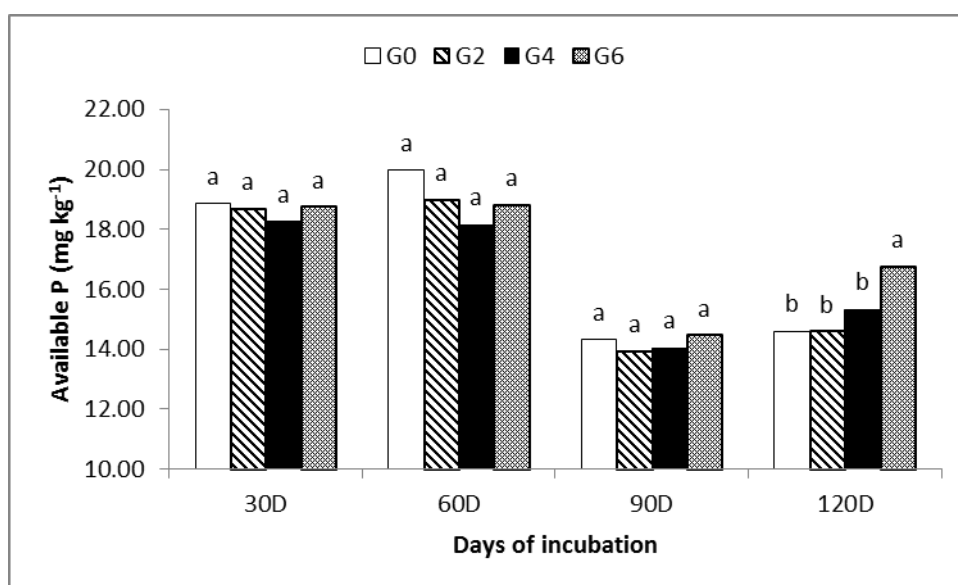


Figure 3.12 Changes of available P on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.3.9 Effect of GML on Si

Figure 3.13 shows the effect of GML on silicon (Si) content at 30, 60, 90 and 120 days of incubation.

At 30 days of incubation, untreated soil was significantly increased Si compared to soil treated with 4 t ha⁻¹ GML. No significant effect was observed between untreated soil, soil treated with 2 and 6 t ha⁻¹ GML and between soils treated with 2, 4 and 6 t ha⁻¹ GML. The value of Si content were 30.65, 29.48, 23.86 and 26.58 mg kg⁻¹ for 0, 2, 4 and 6 t ha⁻¹ GML, respectively.

At 60 days of incubation, no significant effect on Si was observed among treatments. The values were 19.97, 18.97, 18.15 and 18.06 mg kg⁻¹ for 0, 2, 4 and 6 t ha⁻¹ GML, respectively.

At 90 days of incubation, the Si content was increased by 58.28% to 70.02% from 60 days of incubation with values of 59.81, 62.95, 66.36 and 74.13 mg kg⁻¹ for 0, 2, 4 and 6 t ha⁻¹ GML, respectively. No significant effect was observed on Si among treatments.

At 120 days of incubation, soil treated with 6 t ha⁻¹ GML was significantly increased Si content compared to soil treated with 2 t ha⁻¹ GML. The values of Si content were 72.78, 52.06, 74.40 and 79.36 mg kg⁻¹ for 0, 2, 4 and 6 t ha⁻¹ GML, respectively. No significant effect were observed between untreated soil, soil treated with 2 and 4 t ha⁻¹ GML and between untreated soil, soil treated with 4 and 6 t ha⁻¹ GML.

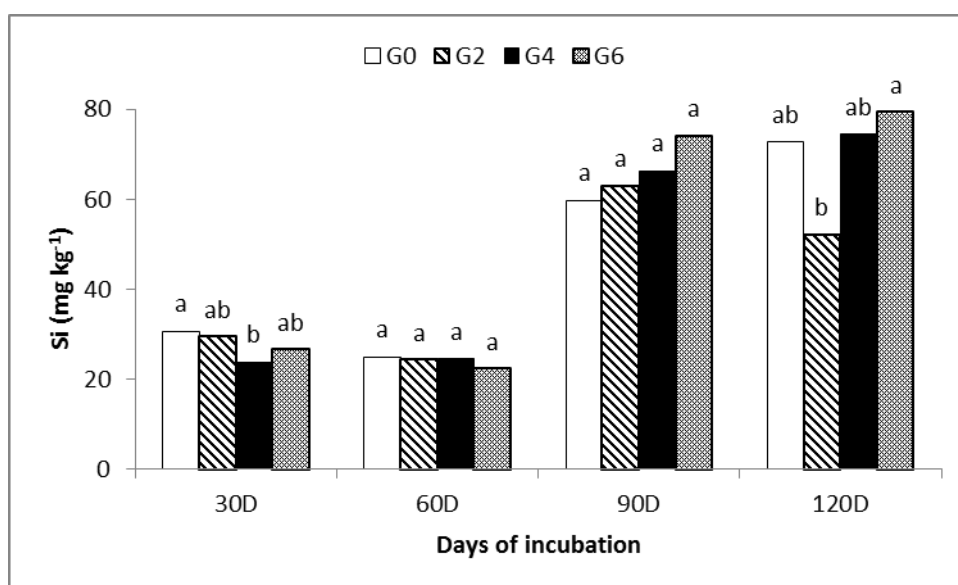


Figure 3.13 Changes of Si content on acidic sulfate soil amended with different rate of ground magnesium limestone (GML). Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's test)

3.4 Discussion

3.4.1 GML as liming material

Under the conditions prevailing in the acidic sulfate soils, silicate minerals in them disintegrate and weather, releasing elements (including Al and Fe). In the soil under study, Al concentration was very high above the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$. Aluminium, whose pKa value is 5.0, had hydrolysed in water to produce protons:



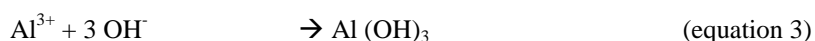
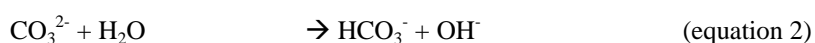
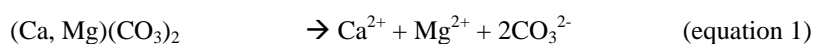
Fe, with a pKa value of 3, had hydrolysed faster and produced more protons than Al. If both Al and Fe are present in the soil, solution pH can be below 3.5, a condition which often occurs in acid sulfate soils.

Acidity of soil can be reduced by applying soil amendments that release anions (OH^-) to neutralize acid protons (H^+ and Al^{3+}) that cause acidification of soil solution. Thus it is necessary to use soil amendments that can release anions (especially, OH^-) to neutralize soil acidity (Rossato et al., 2009; Antonio Nolla et al., 2013) and one particular soil amendment with such a capacity is ground magnesium limestone (GML).

The lime (GML) used in this study was dolomitic limestone ($(\text{Ca}, \text{Mg})(\text{CO}_3)_2$). Adding GML would increase soil pH accordingly, with concomitant addition of Ca and Mg (Table 3.2) into the soil.

Table 3.2 shows the coefficient of linear relationship between rate of GML and soil chemical properties at 30D, 60D, 90D and 120D. Positive relationship was observed for soil pH, exchangeable Ca and Mg. Statically, significant relationship was observed for soil pH and exchangeable at 30D, 60D, 90D and 120D while for exchangeable Mg at 30D, 60D and 120D.

GML ameliorates the soil according to the following reactions:



The GML dissolves into the soil system, 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 neutralize Al by forming inert Al-hydroxides (equation 3). It is also supported by the result from this study as shown in Table 3.2 that the negative relationship was observed for exchangeable Al. Statistically, increasing rate of GML was reduced the exchangeable Al significantly at 30D, 60D, 90D and 120D. In addition, negative relationship was observed for exchangeable Fe. Statistically, increasing rate of GML was reduced the exchangeable Fe significantly at 30D, 60D, 90D and 120D.

Negative relationship was found for exchangeable Na. Statistically, increasing rate of GML was reduced exchangeable Na significantly at 30D. On the other hand, positive relationship was observed for available P. Statistically, increasing rate of GML was increased available P significantly at 120D. No significant relationship was observed for exchangeable K and Si content at 30D, 60D, 90D and 120D.

Table 3.2

R² coefficient of linear relationship between rate of ground magnesium limestone (GML) and selected soil chemical characteristics

Soil chemical characteristics	Days of incubation (D)			
	30D	60D	90D	120D
Soil pH	0.77 **	0.95 **	0.77 **	0.95 **
Exchangeable cations				
Al	-0.90**	-0.94**	-0.77**	-0.91**
Ca	0.92 **	0.99 **	0.64 *	0.92 **
Mg	0.95 **	0.97 **	n.s	0.85 **
Fe	-0.76**	-0.88**	-0.72**	-0.88**
Na	-0.34*	n.s	n.s	n.s
K	n.s	n.s	n.s	n.s
Available cations				
P	n.s	n.s	n.s	0.70 *
Si	n.s	n.s	n.s	n.s

** $p < 0.001$

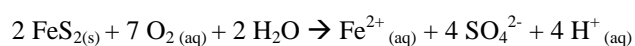
* $p < 0.05$

n.s : not significant

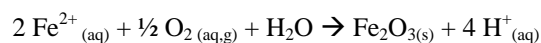
3.4.2 Relationship between soil pH and exchangeable Al

Figure 3.14 shows the relationship between soil pH and exchangeable Al. Soil pH negatively correlates with exchangeable Al. Statistically, significant relationship were observed between soil pH and exchangeable Al at 30D, 60D, 90D and 120D. Soil pH and exchangeable Al showed an antagonistic pattern at 30D, 60D, 90D and 120D; soil pH increased, while exchangeable Al decreased. The line for 90D and 120D were shifted to the below those at 30D and 60D. This implies that days of incubation lower exchangeable Al as the exchangeable Al at 90D and 120D were reduced below critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$ compare to soil incubated at 30D and 60D.

It was noted that line for 90D was shifted to the left from 120D might be caused by the acid released during pyrite oxidation resulted in reducing the soil pH. The following reaction shows on the oxidation of pyrite which produce acidity:



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



Similar findings from Shamshuddin and Auxtero (1991) and Shamshuddin et al. (1995) were noted to promote acidity in acidic sulfate soils. Furthermore, Shamshuddin et al. (2004) found that the soil pH in Cg horizon was lowered by 1 unit after 12 weeks of incubation.

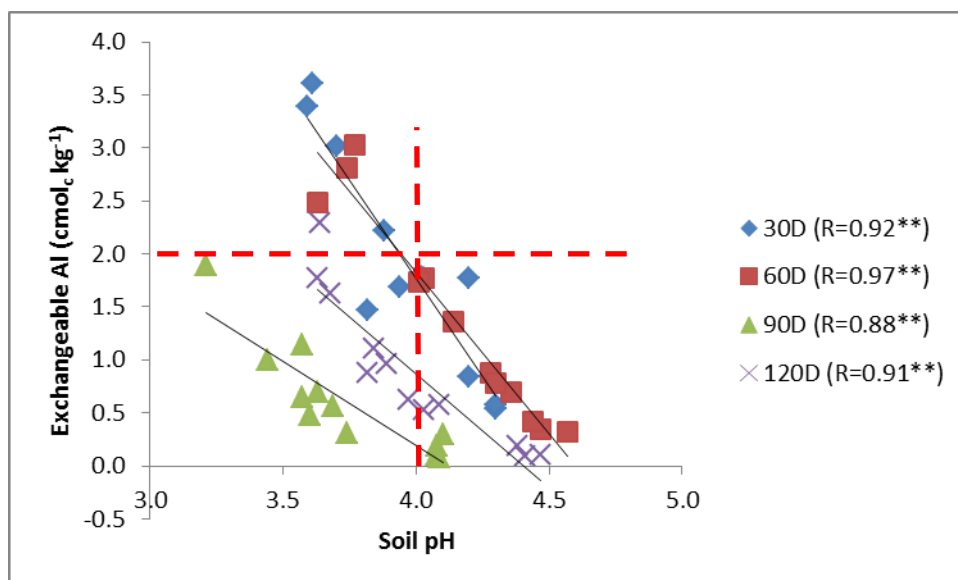


Figure 3.14 Relationship between soil pH and exchangeable Al (** $p < 0.01$). Red lines indicate the recommended level

3.4.3 Relationship between soil pH and exchangeable Ca

Figure 3.15 shows the relationship between soil pH and exchangeable Ca. Soil pH positively correlates with exchangeable Ca. Statistically, significant relationships were observed between soil pH and exchangeable Ca at 30D, 60D and 120D. Soil pH and exchangeable Ca show synergistic patterns at 30D, 60D, 90D and 120D; soil pH increased, while exchangeable Ca increased. The soils treated at 30D, 60D and 120D were above the recommended level of exchangeable Ca value of $2 \text{ cmol}_c \text{ kg}^{-1}$.

The line for 90D was below those at 30D, 60D and 120D. This implies that pyrite oxidation occurs in acidic sulfate soil. Thus, the soil pH and exchangeable Ca were further decreased. Most of the treated soils at 90D were below the recommended level of exchangeable Ca than $2 \text{ cmol}_c \text{ kg}^{-1}$.

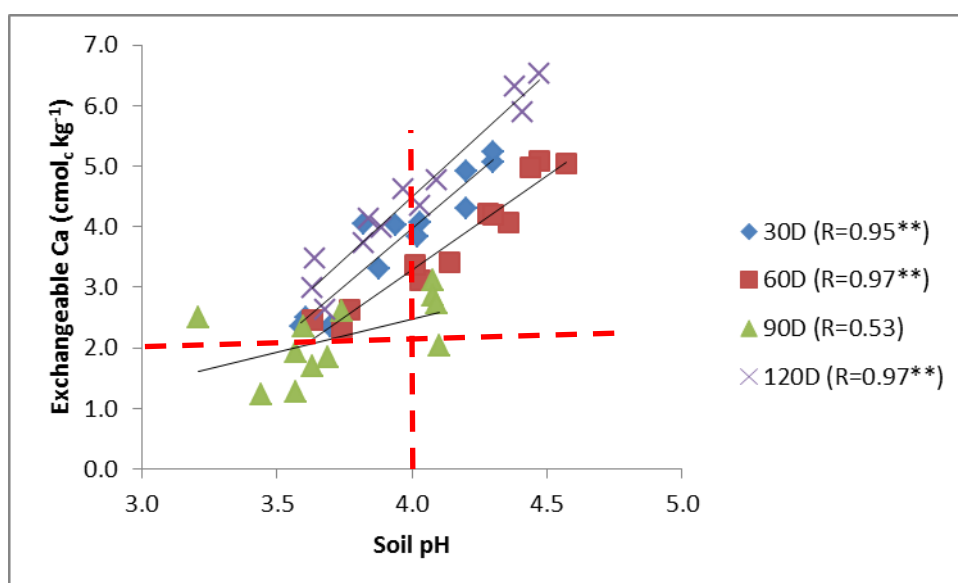


Figure 3.15 Relationship between soil pH and exchangeable Ca (** $p < 0.01$). Red lines indicate the recommended level.

3.4.4 Relationship between exchangeable Al and exchangeable Ca

Figure 3.16 shows the relationship between exchangeable Al and exchangeable Ca at 30D, 60D, 90D and 120D. Exchangeable Al negatively correlates with exchangeable Ca. Statistically, significant relationship were observed between exchangeable Al and exchangeable Ca at 30D, 60D and 120D. Exchangeable Al and exchangeable Ca show an antagonistic pattern; exchangeable Al increased, while exchangeable Ca decreased. Though some treatments of the soil at 30D, 60D and 120D were above the critical level for exchangeable Al value of $2 \text{ cmol}_c \text{ kg}^{-1}$, all treatments were above the recommended level for exchangeable Ca value of $2 \text{ cmol}_c \text{ kg}^{-1}$.

The line for 90D was below those at 30D, 60D, and 120D. Though some of the treatments were below the recommended level for exchangeable Ca below $2 \text{ cmol}_c \text{ kg}^{-1}$, all the treatments were below critical level for exchangeable Al value of $2 \text{ cmol}_c \text{ kg}^{-1}$.

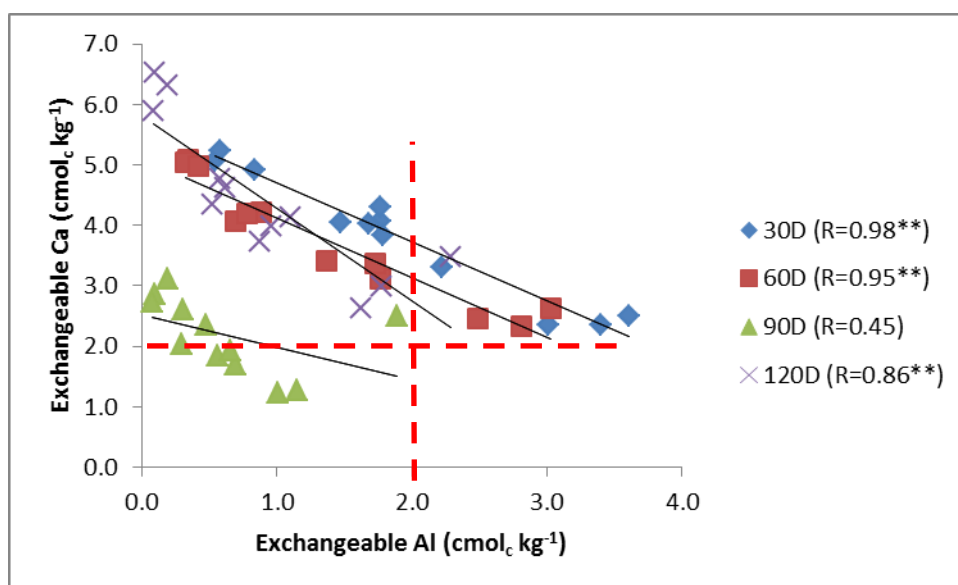


Figure 3.16 Relationship between exchangeable Al and exchangeable Ca (** $p < 0.01$). Red lines indicate the recommended level.

3.4.5 Possibility reduction of GML from common practice

Currently farmers are using GML at rate of 4 t ha^{-1} to ameliorate the acidic sulfate soil before start rice planting. However, based on the personal communication with farmers at respective area, some of affordable farmers were preferred to apply more GML ($> 4 \text{ t ha}^{-1}$) onto their rice field because there are believed that the soil will be better hence produce high rice yield. On the other hand, some farmers that less affordable were not apply any liming materials or apply less than 4 t ha^{-1} GML. In addition, 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} . Therefore, in this chapter we would like to examine the effect of different rate of GML on acidic sulfate soil and also to seek the possibility in reducing the GML rate from common practice of 4 t ha^{-1} .

The effect of GML on acidic sulfate soil was evaluated based at 30 days of incubation (30D). There are two reasons to focus on the data from the 30D. First, the Al acidity gradually decreases in soil (Al_{soil}) and water (Al_{water}) as shown on Figure 3.17. This will support positive crop growth inline with vegetative, reproductive and flowering of rice growth phases. The critical level for Al in soil is $2 \text{ cmol}_c \text{ kg}^{-1}$ (Hiradate et al., 2007) and water is 2 mg L^{-1} (Dobermann and Fairhurst, 2000). At 30D, only untreated soil was above the Al critical level in the soil and water. At 60D, 90D and 120D, all treatments were below the critical level except for soil treated with 6 t ha^{-1} GML was above the critical level of Al in water. Second, it is more practical and applicable by the local farmers compared to 60D, 90D and 120D because 30D is more time-suitable for them otherwise they need to wait too long.

The effect of GML on acidic sulfate soil was evaluated considering the guideline for soil chemical characteristics to achieve good rice growth suggested by past studies. The following are each guideline of soil chemical characteristics used in this study.

- a) Soil pH $>$ (Shamshuddin, 2006)
- b) Exchangeable Al $< 2 \text{ cmol}_c \text{ kg}^{-1}$ (Hiradate et al., 2007)
- c) Exchangeable Ca $> 2 \text{ cmol}_c \text{ kg}^{-1}$ (Palhares de Melo et al., 2001)
- d) Exchangeable Mg $> 1 \text{ cmol}_c \text{ kg}^{-1}$ (Dobermann and Fairhurst, 2000)
- e) Exchangeable K $> 0.2 \text{ cmol}_c \text{ kg}^{-1}$ (Dobermann and Fairhurst, 2000)
- f) Fe content $> 2 \text{ mg kg}^{-1}$ (Dobermann and Fairhurst, 2000)
- g) Available P 7-20 mg kg^{-1} (Dobermann and Fairhurst, 2000)
- h) Si content $> 43 \text{ mg kg}^{-1}$ (Sarayanawamy and Prakash, 2009)

Table 3.3 shows the effect of GML on chemical soil properties at 30D. Treatments in yellow color indicated that it achieved the recommended level.

For the soil pH, soil treated with 6 t ha⁻¹ GML achieved the recommended level more than 4 while for exchangeable Al, soil treated with 2, 4 and 6 t ha⁻¹ GML were below the critical level of 2 cmol_c kg⁻¹. On the other hand, for exchangeable Ca, Mg, K and available P, all treatments were achieved the recommended level of more than 2, 1, 0.2 cmol_c kg⁻¹ and ranged between 7-20 mg kg⁻¹, respectively. Furthermore, for Fe content, the untreated soil and soil treated with 1 t ha⁻¹ GML were above the recommended level of 2 mg kg⁻¹. For the Si content, all treatments were not meeting the recommended level of 43 mg kg⁻¹. Finally, it shows that untreated soil and soil treated with 4 t ha⁻¹ GML achieved the recommended level of 5 soil chemical characteristics out of 8 while soil treated with 2 and 6 t ha⁻¹ GML achieved the recommended level 6 out of 8 (marked with yellow color). For untreated soil, the soil pH, exchangeable Al and Si content were not meeting the recommended level. For soil treated with 1 t ha⁻¹ GML, the soil pH and Si content were not meeting the recommended level. For the soil treated with 4 t ha⁻¹ GML, the soil pH, Fe content and Si content were not meeting the recommended level. For soil treated with 6 t ha⁻¹ GML, Fe content and Si content were not meeting the recommended level.

Though untreated soil and soil treated with 4 t ha⁻¹ GML achieved similar recommended level 5 out of 8, we will not consider untreated soil as a good approach. This is because, the soil pH was 3.63 below than 4 and also exchangeable Al was 3.34 above 2 cmol_c kg⁻¹. It means that untreated soil is still toxicity which it is not suitable for crop as it will inhibit the root growth. Though the recommended soil pH of 4 was not achieved for soil treated with 4 t ha⁻¹ GML, the value 3.98 was very close to 4.

On the other hand, soil treated with 2 and 6 t ha⁻¹ GML achieved similar recommended level 6 out of 8. Though the soil pH for soil treated with 6 t ha⁻¹ GML was 4.26 above 4, the exchangeable Al was still above the critical level of 2 cmol_c kg⁻¹ even the Al in water was below than critical level of 2 mg L⁻¹ as shown in Figure 3.17. The exchangeable Al for soil treated with 6 t ha⁻¹ GML was above the critical level of 2 cmol_c kg⁻¹ at 60D, 90D and 120D (Figure 3.18) and this is inline with vegetative, reproductive flowering phase which will affect on the crop growth. In addition, 6 t ha⁻¹ GML was above the rate of current practice of 4 t ha⁻¹ in Malaysia now which means the cost would be increased than now. Thus, 6 t ha⁻¹ GML was not recommended for the farmers in Malaysia to improve the acidic sulfate soil.

Though the recommended soil pH of 4 was not achieved for soil treated with 2 t ha⁻¹ GML, the value 3.97, was very close to 4. This value also very close the soil pH for soil treated with 4 t ha⁻¹ GML which is common rate use currently by the farmers. In comparison to common practice of 4 t ha⁻¹ GML, soil treated with 2 t ha⁻¹ GML show the sufficient Fe content value 3.93 mg kg⁻¹ above the recommended value of 2 mg kg⁻¹. In addition, both treatments of 2 and 4 t ha⁻¹ GML achieved recommended value of chemical soil properties for exchangeable Al, Ca, Mg, K and available P. Thus, 2 t ha⁻¹ GML show a promising recommendation compare to others treatments. This recommendation rate will add value to the cost input which means the farmers are able to reduce about approximately 50% from the current cost as the rate of GML show the possibility reduce from 4 t ha⁻¹ to 2 t ha⁻¹.

Table 3.3

Effect of GML on chemical soil properties at 30D. Means marked with the same letter for each chemical soil properties are not significantly different at $p<0.05$

Chemical soil properties	Recommended level	GML (t ha ⁻¹)			
		0	2	4	6
Soil pH	>4	3.63 ^a	3.97 ^a	3.98 ^a	4.26 ^a
Exch-Al	<2	3.34 ^a	1.92 ^b	1.64 ^b	0.65 ^c
Exch-Ca	>2	2.40 ^c	3.73 ^b	4.12 ^b	5.07 ^a
Exch-Mg	>1	3.13 ^c	3.79 ^b	4.16 ^b	4.84 ^a
Exch-K	>0.2	0.47 ^a	0.54 ^a	0.51 ^a	0.55 ^a
Available P	7-20	18.18 ^a	18.67 ^a	18.25 ^a	18.74 ^a
Fe content	>2	9.63 ^a	3.93 ^b	1.09 ^c	1.76 ^c
Si content	>43	30.65 ^a	29.48 ^{ab}	23.86 ^b	26.58 ^{ab}

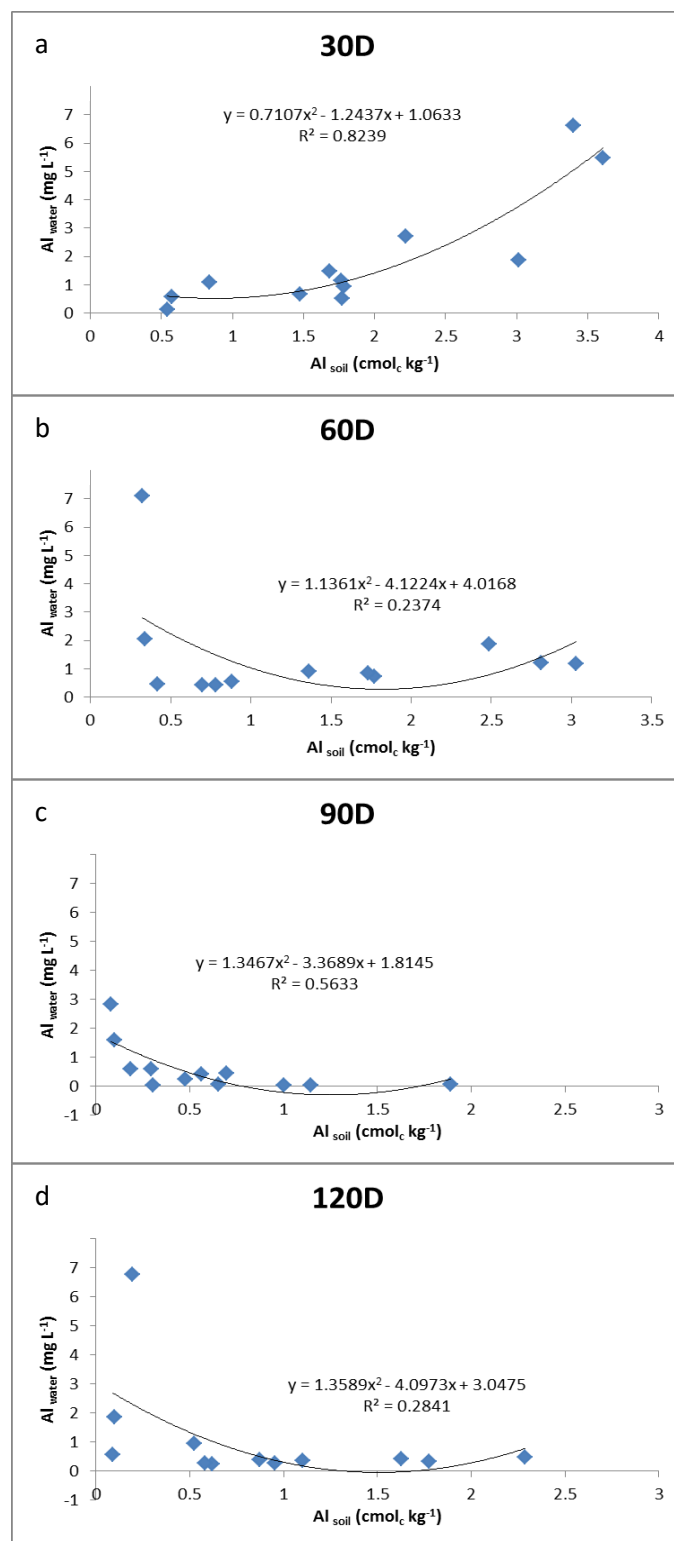


Figure 3.17 Relationship between Al content in the soil (Al_{soil}) and Al content in water (Al_{water}) after 30D (a), 60D (b), 90D (c) and 120D (d). n=12 for each days of incubation (4 treatments x 3 replications)

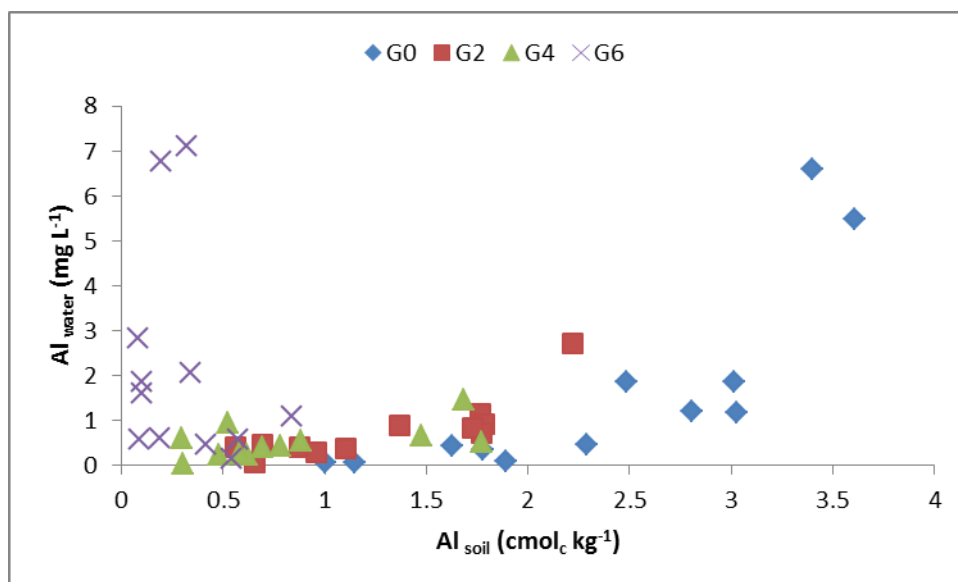


Figure 3.18 Relationship between Al_{water} and Al_{soil} for entire treatments throughout incubation period

3.4 Conclusion

From the study it show that possibility in reduction of GML rate of 2 t ha⁻¹ from the common rate currently use in Malaysia at 4 t ha⁻¹. 2 t ha⁻¹ GML achieved the recommended value for exchangeable Al, Ca, Mg, K available P and Fe content. It is also able to reduce the cost of GML by 50% from the common rate use by the farmers in Malaysia now at 4 t ha⁻¹ GML.

In addition, application of GML was recommended 30 days before planting as the Al in the soil and water were gradually decreased after 30 days of incubation.

Chapter 4 Alleviating aluminum toxicity in an acidic sulfate soil by calcium silicate application

4.1 Introduction

Soils are the key to understand the earth System as they control the hydrological, biological, geochemical and erosional cycles (Smith et al., 2015; Decock et al., 2015; Keesstra et al., 2012). Moreover, the soil system is damaged by millennia use and abuse of the soil resources, and the soils are failing to supply the human kind with goods and services due to the degradation of the soil structure, lost of soil quality and soil fertility (Dai et al., 2015; Masto et al., 2015; Zhao et al., 2015; Cerda, 1998; Costa et al., 2015). Pollution is one of the triggering factors of soil degradation and it is a worldwide problem (Wang et al., 2015; Roy and Mcdonald, 2015; Mahmoud and Abd El-Kader, 2015). Therefore, this is why it is necessary to develop a new strategy to restore and rehabilitate the soils, which can be based on the use of amendments (Riding et al., 2015; Hu et al., 2015; Yazdanpanah et al., 2016; Tejada and Benitez, 2014; Prosdocimi et al., 2016).

The application of soil amendments to acidic soil is a common approach for improving fertility. Suswanto et al. (2007), Shamshuddin et al. (2009), Shazana et al. (2013), Elisa et al. (2014), Fernandez-Sanjurjo (2014) and Rosilawati et al. (2014) reported that the infertility of acidic soils can be ameliorated by application of lime, basalt, gypsum, biochar, controlled-release fertilizer, organic fertilizer, and/or their combination at an appropriate rate. Application of these ameliorants increased soil pH and reduced Al toxicity, resulting in improved rice growth. In addition to these improvements, these ameliorants also supply calcium (Ca) and magnesium (Mg), which are needed for crop growth and development.

Besides Ca and Mg, silicon (Si) is also important for rice growth. It has a positive effect on the growth of crops such as tomato (Peaslee and Frink, 1969), barley and soybean (Hodson and Evans, 1995; Nolla et al., 2006), and many others (Liang et al., 2007; Nolla et al., 2012). The application of Si may reduce the severity of fungal diseases such as blast and sheath blight of rice (Farnaz Abed-Ashtiani et al., 2012); powdery mildew of barley, wheat, cucumber, muskmelon, and grape leaves; and vermin damage of rice by plant hopper (Crock and Prentice, 2012; Ma et al., 2001; Menzies et al., 1992; Bowen et al., 1992; Datnoff et al., 2001). In addition, Si can effectively reduce Al toxicity (Barcelo et al., 1993). Calcium silicate application could be a source of Si for soil-crop interactions.

Ground magnesium limestone (GML) is a common soil amendment and the effect of GML on acidic sulfate soil have been presented in Chapter 3, however increase in price and labor cost tends to shift the focus towards using other alternative, such alternative is calcium silicate slag fertilizer. It originates from steel slag which is a steel-making industrial by-product. Many countries (i.e Japan, Germany and Italy) have used this by product in the agriculture sector for rice, sugar cane and other crop production.

In Malaysia, calcium silicate slag is classified as SW 104; metal and metal bearing wastes, under Malaysia law of Environmental Quality Act 1974, First Regulation (Schedule 2). Under the regulation, direct application of the calcium silicate slag onto the soil in Malaysia is not allowed. Thus, chemical grade calcium silicate was used in this experiment. In addition to that, industrial by-product such as calcium silicate slag that treated as waste in Malaysia can be recycled; this add value of the whole industry and agriculture sector in Malaysia.

The objective of this study was to evaluate the ameliorative effect of calcium silicate on acidic sulfate soil in Malaysia as an alternative to GML.

4.2 Materials and methods

4.2.1 Soil type, treatments, and experimental design

Details about soils used in this experiment have been explained in section 3.2.1.

Five hundred grams of soil was used to fill a plastic pot, which was then incubated for 120 days. The treatments included 0 (CS0), 1 (CS1), 2 (CS2), and 3 (CS3) t ha⁻¹ of calcium silicate, with three replications. These were arranged in a completely randomized design (CRD). The total number of samples was 48 (4 treatments × 3 replications × 4 sampling times). Twelve pots were sampled every 30 days throughout the incubation period, i.e., the sampling times were at 30 days (30D), 60 days (60D), 90 days (90D), and 120 days (120D) of incubation and corresponded to the vegetative, reproductive, flowering, and maturity phases of rice growth, respectively. The calcium silicate (CaSiO₃) used in this experiment was obtained from Kaolin (Malaysia) Sdn. Bhd., Malaysia. This calcium silicate had the following composition: SiO₂ = 40–55%, calcium (as CaO) = 40–50%, Al₂O₃ = below 1.5%, MgO = below 3%, iron (as Fe₂O₃) = below 1%, and pH = 8.54.

The soils were mixed thoroughly with the added calcium silicate prior to the addition of water. Tap water was added regularly and the water levels were maintained at approximately 5 cm (height) above the soil surface. The composition of the tap water in relation to phosphorus (P), potassium (K), aluminum (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. The pH of the tap water used was 7.37.

4.2.2 Soil analyses

Soil samples were air-dried, ground, and passed through a 2 mm sieve prior to chemical analyses. Soil pH was determined in water at a ratio of 1:2.5 (soil/distilled water) using a glass electrode pH meter (Metrohm 827 pH meter). Total C, N, and S were determined using a CNS analyzer Leco RC-412 C Leco Corporation, St. Joseph, MI.. Cation exchange capacity (CEC) was determined using 1 M NH₄OA_c at pH 7 (Chapman, 1965). Exchangeable Ca, Mg, K, and Na were determined using 1 N NH₄Cl (Ross and Ketterings, 1995; Shamshuddin, 2006). To achieve this, 2 g of air-dried soil was placed in a 50 mL centrifuge tube and 20 mL 1 N NH₄Cl was added. The sample was shaken for 2 h on an end-to-end shaker at 150 rpm, followed by centrifugation at 2500 rpm for 15 min. The extract was passed through a filter paper Whatman No. 42 into a 50 mL plastic vial. The exchangeable Ca, Mg, K, and Na in the extract were determined by inductively coupled plasma-optical emission

spectroscopy (ICP-OES) (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA). Exchangeable Al was determined by extracting 5 g of soil with 50 mL of 1 M KCl. The mixture was shaken for 30 min and the extracted Al was analyzed by ICP-OES (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA). Extractable Fe, Cu, Zn, and Mn were extracted using extracting agent (0.05 N HCl and 0.025 N H₂SO₄). To achieve this, 5 g of air-dried soil was shaken with 25 mL of extracting agent for 15 min. The extract was passed through a filter paper Whatman No. 42 and used to determine Fe, Cu, Zn, and Mn by atomic absorption spectrometry (AAS) Perkin Elmer, model 1100B. Additionally, 0.01 M CaCl₂ was used to extract plant-available Si from the soil. For this, 2 g of soil was shaken for 16 h with 20 mL CaCl₂ extractant in a 50 mL centrifuge tube on an end-to-end shaker. The sample was centrifuged at 2000 rpm for 10 min before the supernatant was filtered through a filter paper Whatman No. 42 and analyzed for Si (Narayanaswamy and Prakash, 2009) using ICP-OES (Optima 8300 ICP-OES, Perkin Elmer, Waltham, MA, USA).

4.2.3 Statistical analysis

Statistical analysis for means comparison was performed using Tukey's test in SAS version 9.2 (SAS, Institute, Inc., Cary, NC).

4.3 Results

Changes of selected chemical soil characteristics on acidic sulfate soil amended with different rate of calcium silicate (0, 1, 2 and 3 t ha⁻¹) are shown in Figure 4.1 until Figure 4.4. The soil chemical characteristics are soil pH, exchangeable Al, exchangeable Ca and Si content. The effect of calcium silicate rate applied was compared for each days of incubation. 30, 60, 90 and 120 days of incubation represent rice phase of vegetative, reproductive, flowering and maturity, respectively. The means marked with the same letter for each days of incubation are not significantly different at $p < 0.05$ (Tukey's Test)

4.3.1 Initial soil chemical characteristics

Initial soil pH and exchangeable Al were 2.90 and 4.26 cmol_c kg⁻¹, respectively. Exchangeable Ca, Mg, K, and Na were 1.68, 2.61, 0.55, and 2.61 cmol_c kg⁻¹, respectively. Al saturation was 28%. Total C, N, and S were 3%, 0.2%, and 0.13%, respectively. At the site where the soil was sampled, rice is normally grown twice a year and the straw is often left to rot on the paddy field. The decomposition of the rice straw, to some extent, contributed to the increased C content and CEC of the soil. In this study, the CEC of the soil was 18.12 cmol_c kg⁻¹. The values for extractable Fe, Cu, Zn, Mn, and Si prior to incubation were 1118.6, 0.23, 0.96, 1.60, and 21.21 mg kg⁻¹, respectively.

4.3.2 Effect of calcium silicate on soil pH

Figure 4.1 shows the effect of calcium silicate application on soil pH under the submerged conditions. It shows that soil pH increased in line with the incremental increases in the calcium silicate application rate. The highest soil pH increase was from 2.90 (initial) to 3.95 due to the application of 3 t ha⁻¹ calcium silicate. At 30 days of incubation (30D), soil pH of CS2 was significantly higher than that of CS1, with values of 3.77 and 3.62, respectively. Treatment CS3 was significantly higher in terms of soil pH compared with CS0, CS1, and CS2 at 60D; CS0 and CS1 at 90D; and CS0, CS1, and CS2 at 120D, showing values of 3.90, 3.84, and 3.95, respectively.

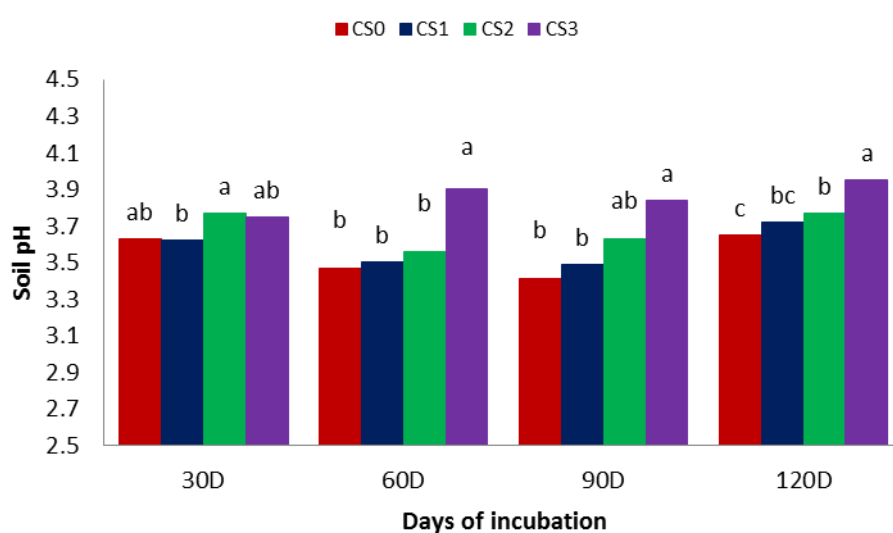


Figure 4.1 Effects of calcium silicate application on soil pH under submerged conditions. Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's Test)

4.3.3 Effect of calcium silicate on exchangeable Al

Figure 4.2 shows the effect of calcium silicate application on exchangeable Al. It shows that as the calcium silicate rate increased, the exchangeable Al decreased from 4.26 (initial) to 0.82 $\text{cmol}_c \text{ kg}^{-1}$. This is a 74% decrease in exchangeable Al due to the application of calcium silicate. At 30D and 120D, exchangeable Al content in the soil treated with 2 and 3 t ha^{-1} of calcium silicate had significantly decreased compared to that in the untreated soil. However, there was no significant effect of calcium silicate on exchangeable Al at 60D and 90D days of incubation.

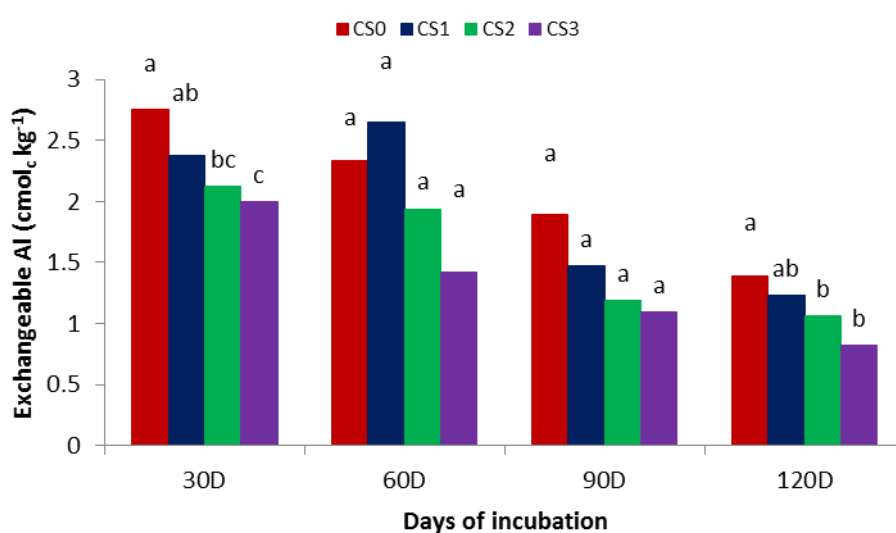


Figure 4.2 Effects of calcium silicate application on exchangeable aluminum. Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's Test)

4.3.4 Effect of calcium silicate on exchangeable calcium

Figure 4.3 show that the application of calcium silicate increased exchangeable Ca. There was a significant effect among the treatments at 30D. At 60D, 90D, and 120D, soil treated with 2 and 3 t ha⁻¹ of calcium silicate had significantly increased soil-exchangeable Ca compared with both untreated soil and soil treated with 1 t ha⁻¹ of calcium silicate. No significant effect was observed between CS0 and CS1 at 60D, 90D and 120D. The exchangeable Ca was increased from 1.68 cmol_c kg⁻¹ (initial) to 4.94 cmol_c kg⁻¹ (highest)

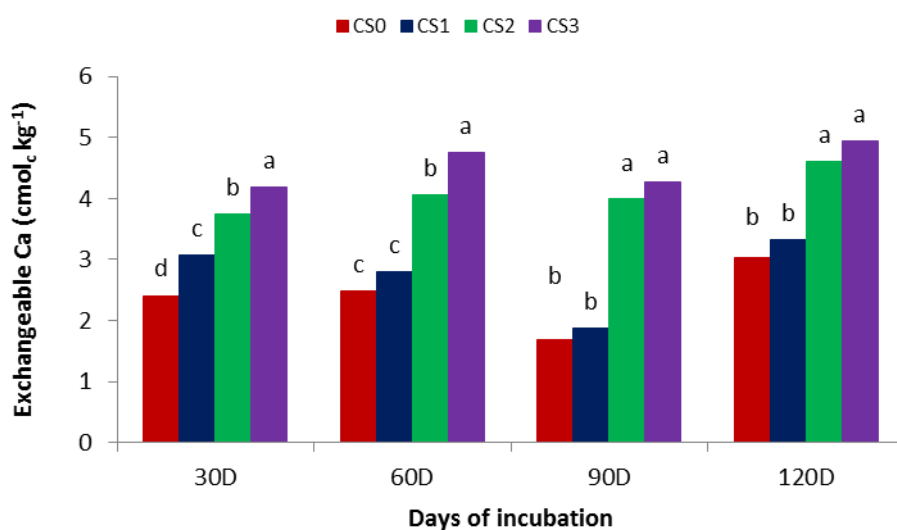


Figure 4.3 Effects of calcium silicate application on exchangeable calcium. Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's Test)

4.3.5 Effect of calcium silicate on silicon content

Application of calcium silicate increased the Si content of the soil, as shown in Figure 4.4, from 14% to 74%. At 30D, soil treated with 2 and 3 t ha⁻¹ of calcium silicate had a significantly increased Si content compared with both untreated soil and soil treated with 1 t ha⁻¹ of calcium silicate. At 60D, the Si content increased significantly for soil treated with 1, 2 and 3 t ha⁻¹ of calcium silicate compared with untreated soil. The Si content of the soil continued to increase at 90D; in the soil treated with 1 t ha⁻¹ calcium silicate, it was significantly increased compared to the 2 t ha⁻¹ treatment. However, no significant effect was observed among the treatments at 120D.

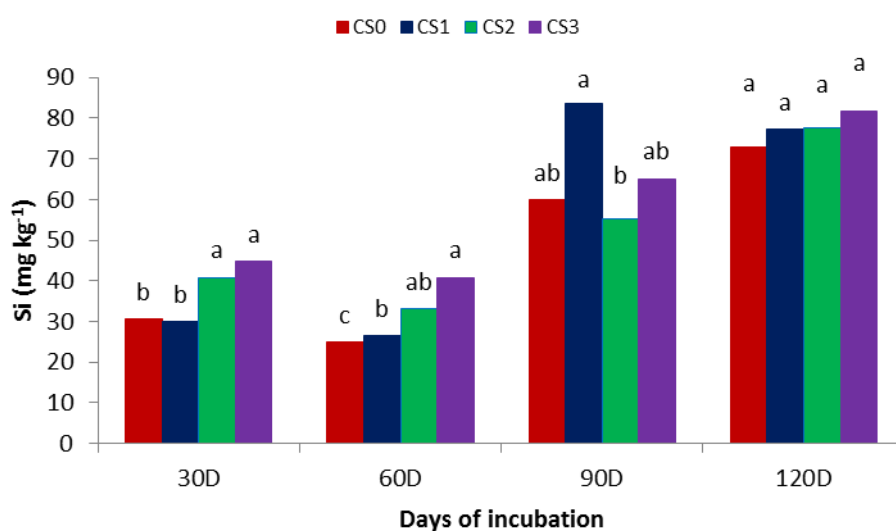


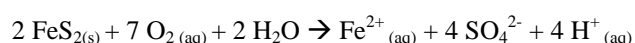
Figure 4.4 Effects of calcium silicate application on silicon content. Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's Test)

4.4 Discussion

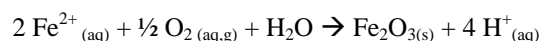
4.4.1 Soil pH changes

From this study, it was found that calcium silicate can neutralize H^+ ions in soil, as noted by the pH increase in acidic soils upon calcium silicate application (Figure 4.1). Similar findings have been found by Smyth and Sanchez (1980) and Fiantis et al. (2002). These authors attributed their results to the OH^- released from colloidal surfaces during the adsorption of the silicate ions. Due to the application of calcium silicate, soil pH increased significantly from 2.90 (initial) to 3.41–3.95. During the incubation period, there was a strong relationship between calcium silicate and soil pH at 30D ($R^2 = 0.77$), 60D ($R^2 = 0.77$), 90D ($R^2 = 0.84$), and 120D ($R^2 = 0.92$). The increasing correlation coefficient over time was related to the increasing capacity of the soil to adsorb silicate anions.

It was observed that the soil pH was slightly lower for CS0, CS1, and CS2 at 60D and 90D compared to that at 30D and 120D. The decrease in soil pH is believed to be due to the release of protons as pyrite in the soil was oxidized during the incubation period. Shamshuddin et al. (2004) reported that after 12 weeks of incubation, soil pH in the Cg horizon was lowered by 1 unit. The results from the current study are consistent with those from other studies on acidic soils (Shamshuddin and Auxtero, 1991; Shamshuddin et al., 1995; Shamshuddin et al., 2014). The oxidation of pyrite, which produces acidity, may have taken place according to the following reactions outlined by van Breemen (1976):



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



4.4.2 Amelioration of Al toxicity

As the soil pH increased due to the application of calcium silicate, exchangeable Al decreased to below the critical level for rice growth of $2 \text{ cmol}_c \text{ kg}^{-1}$ (Hiradate et al., 2007). Figure 4.2 shows the effect of the treatments on exchangeable Al. It shows that exchangeable Al decreased significantly among the treatments at 30D and 120D. At 30D, the exchangeable Al contents of treatments CS2 and CS3 were significantly reduced compared to CS0 values of 2.12 and $2 \text{ cmol}_c \text{ kg}^{-1}$, respectively. These values were near the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$. It is also shown that exchangeable Al decreased further as the incubation period was further extended. Figure 4.5 shows the relationship between exchangeable Al and soil pH, where the lines for 60D, 90D, and 120D are below the line for 30D. This implies that a prolonged incubation period would further reduce the exchangeable Al content. The decrease in Al could also be due to the precipitation of Al in the form of inert Al-hydroxides. The exchangeable Al content was reduced to below the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$ at 90D and 120D.

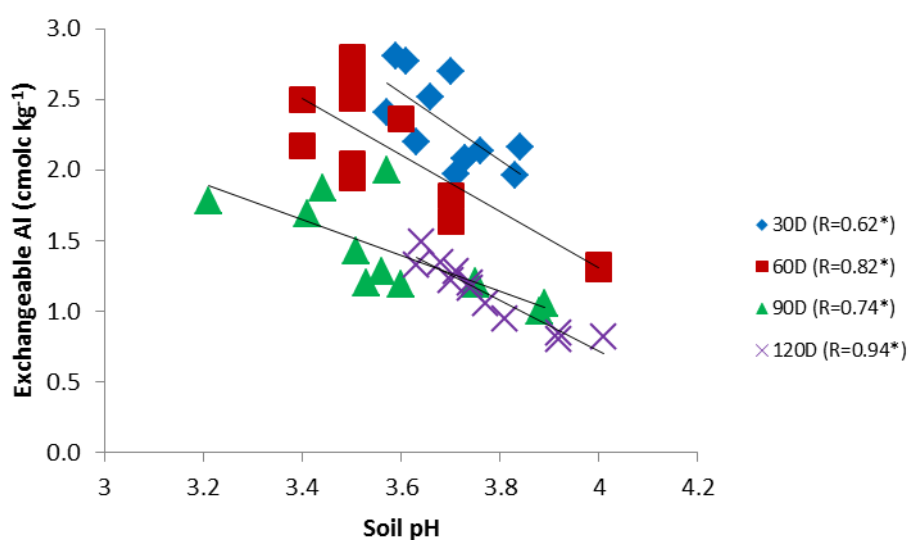


Figure 4.5 Relationship between exchangeable Al and soil pH (* $p < 0.05$)

The reduction in exchangeable Al is explained as follows. It is possible that soil Al can be reduced by the reactions of Si-rich compounds. By such reactions, Datnoff et al. (2001) postulated five mechanisms of Al reduction: 1) monosilicic acids increase soil pH (Lindsay, 1979); 2) monosilicic acids are adsorbed on Al hydroxides, reducing their mobility (Panov et al., 1982); 3) soluble monosilicic acid forms slightly soluble substances with Al ions (Lumsdon and Farmer, 1995); 4)

mobile Al is strongly adsorbed on silica surfaces (Schulthess and Tokunaga, 1996); and 5) mobile silicon compounds increase plant tolerance to Al (Rahman et al., 1998). All of these mechanisms may work simultaneously, with one perhaps prevailing under certain soil conditions (Dantoff et al., 2001).

As the exchangeable Al decreased, Al saturation decreased (Figure 4.6). Al saturation was below 30% for all treatments on entire incubation period. Al saturation decreased gradually with days of incubation. Soil treated with CS2 and CS3 significantly decreased Al saturation compared to CS0 and CS1 at 30D and 60D while untreated soil was significantly high in Al saturation compared to treated soil at 90D and 120D.

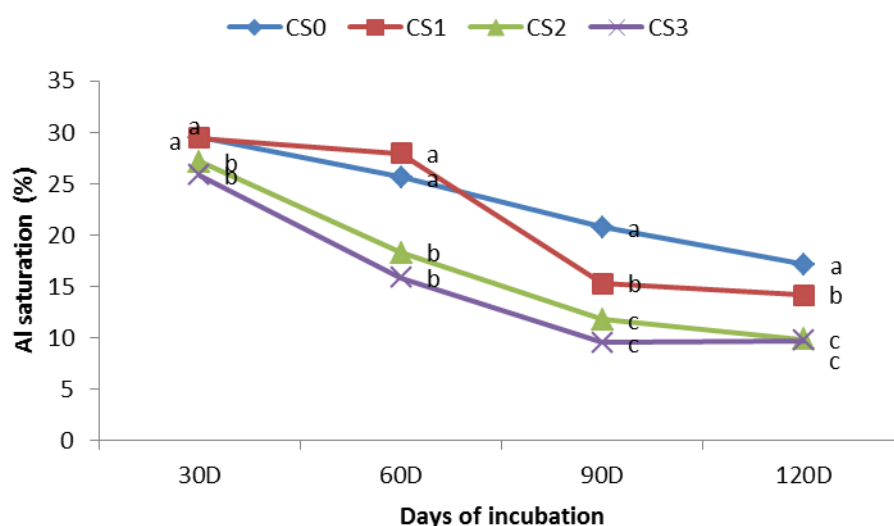
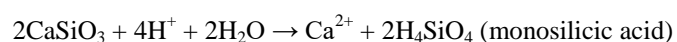


Figure 4.6 Effects of calcium silicate application on aluminium saturation. Means marked with the same letter for each incubation day are not significantly different at $p < 0.05$ (Tukey's Test)

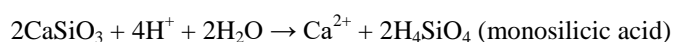
The silicate anion can also neutralize H^+ in the soil solution. As the silicate anion captures H^+ ions, it forms monosilicic acid (H_4SiO_4), as shown in the equation below:



Monosilicic acid could complex with Al^{3+} in the soil solution to form non-toxic aluminosilicate and hydroxyl-alumino-silicate compounds, which precipitate in the root zone. This reaction would reduce Al toxicity in rice grown on acidic soils treated with calcium silicate (Hodson and Evans, 1995; Miranda, 2012).

4.4.3 Calcium content

Furthermore, the application of calcium silicate to the acidic soil showed an immediate ameliorative effect, i.e., the Ca content increased from 1.68 (initial) to above the critical level of 2 $\text{cmol}_c \text{ kg}^{-1}$ (Palhares de Melo et al., 2001) at 30D. Increasing the rate of calcium silicate increased the Ca content of the soil significantly (Figure 4.3). For treatment CS3, exchangeable Ca increased significantly compared to CS0 and CS1 throughout the incubation period, with increases of 42.48%, 47.78%, 60.65%, and 38.66% after 30D, 60D 90D and 120D, respectively. However, no significant difference was observed between treatments CS2 and CS3 at D90 and D120. Treatment CS1 was significantly increased compare to CS0 at 30D while treatment CS2 was significantly increased at 60D, 90D and 120D. The increment of Ca was come from calcium silicate as shown in the below equation:



In addition to that, Figure 4.7 shows that exchangeable Ca was negatively correlated with exchangeable Al for entire days of incubation. The line was gradually shifted to the left as the incubation day extended. The Al and Ca content showed synergism pattern: Al decreased, while Ca increased. This situation indicates that when Al content of the soil is low, its toxicity may not be the dominant factor inhibiting rice plant growth. Furthermore, Ca is available for plant uptake.

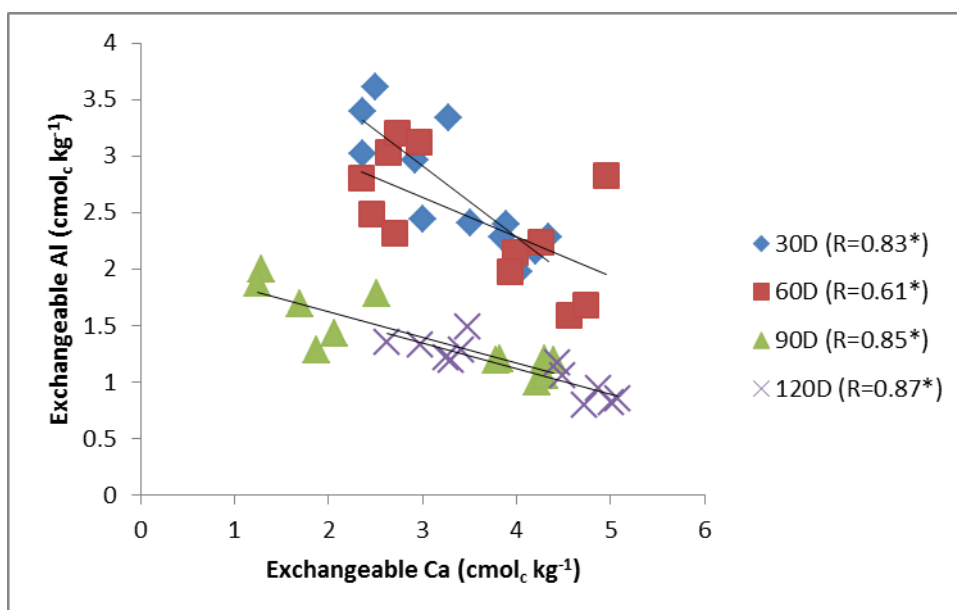


Figure 4.7 Relationship between exchangeable Al and exchangeable Ca (* $p < 0.05$)

4.4.4 Availability of Si

In the current study, the Si content prior to the incubation was 21.21 mg kg^{-1} ; the critical soil Si concentration for crop production is 43 mg kg^{-1} (Narayanaswamy and Prakash, 2009). Figure 4.4 shows the effect of calcium silicate application on Si content. At 30D, the Si content in treatments CS2 and CS3 was significantly higher than in treatments CS0 and CS1. At 60D, treatment CS3 increased the Si content significantly compared to that of CS0 and CS1, with a value of 40.81 mg kg^{-1} Si. In all treatments at 90D and 120D, the Si content of the soil surpassed the deficiency level. At 90D, the Si content of treatment CS1 was significantly higher than that of CS2, with a value of 83.53 mg kg^{-1} . The Si content of the soil was affected by the length of incubation, i.e., the Si content of all treatments further increased at 120 days of incubation.

When the soil pH increased, the Si content of the soil also increased (Figure 4.8). The Si content was positively correlated with soil pH at 30D and 60D, likely due to the dissolution of calcium silicate. The ability of the soil to adsorb Si was higher at 30D and 60D than at 90D and 120D. There was no correlation observed at 90D and 120D, even though the Si content was higher, probably because the soil-exchangeable sites became fully occupied with Si through adsorption processes. This proves that the application of calcium silicate to soil, accompanied by an increase in soil pH, enhances the ability of soil to adsorb Si.

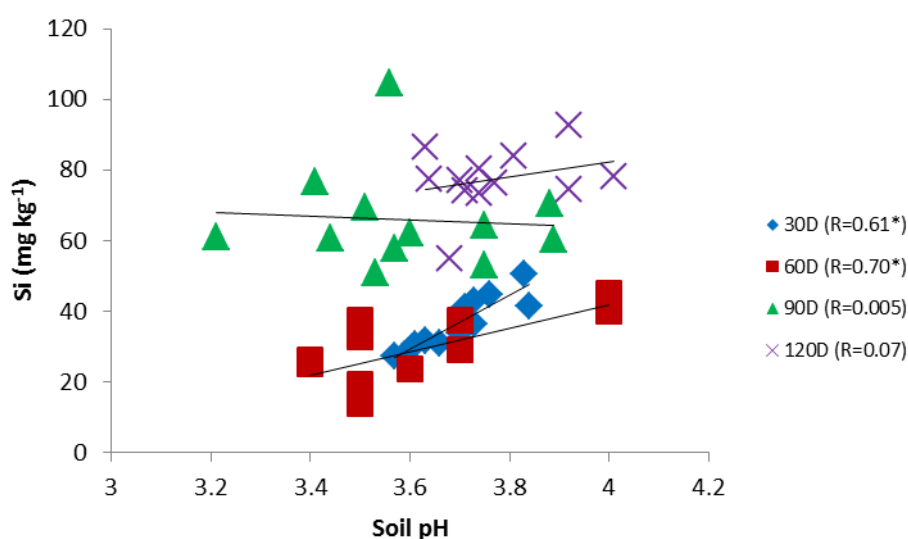


Figure 4.8 Relationship between Si content and soil pH throughout the incubation period (* $p < 0.05$)

The positive effect of the presence of Si at 30D and 60D corresponds with the early growth stage of rice, i.e., the active tillering stage. This means that a rice plant can actively uptake Si during the tillering stage, hence improving rice growth. Figure 4.9 shows the relationship between the exchangeable Al and Si contents of the soil throughout the incubation period after the application of calcium silicate. The reduction in exchangeable Al corresponded directly with the availability of Si in the soil. This means that as more Si is available in acidic soil, a reduction in the exchangeable Al content occurs. Exchangeable Al was negatively correlated with Si content in the soil at 30D ($R = 0.77$) and 60D ($R = 0.92$), whereas no correlation was observed at 90D and 120D. In Figure 4.9, the 60D line is below the 30D line, indicating that as the incubation period increased, the Al and Si contents showed an antagonistic pattern: Al decreased, while Si increased. This phenomenon indicates that when the Al content of the soil is low, its toxicity may not be the dominant factor inhibiting rice plant growth. On the other hand, Si becomes more readily available for plant uptake. Therefore, the recommendation of optimal time to plant rice is 30 days after applying calcium silicate because the exchangeable Al is almost reduced to below the critical value of $2 \text{ cmol}_c \text{ kg}^{-1}$. Because the Si content increased with incubation time, the rice plant could actively uptake Si for growth during active tillering.

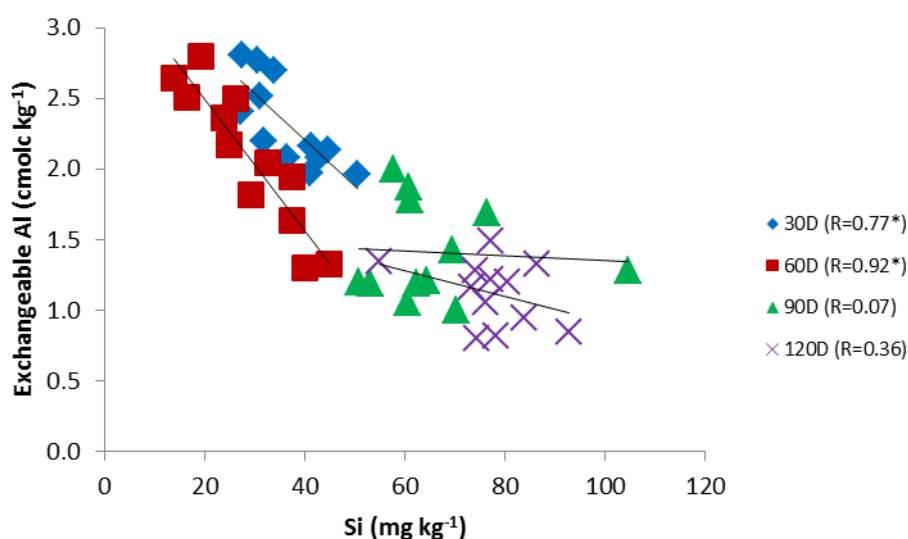


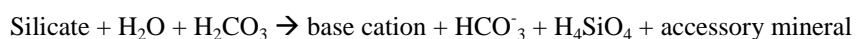
Figure 4.9 Relationship between exchangeable Al and Si content in the soil throughout the incubation period (* $p < 0.05$)

Although Si is not considered as an essential element for plant growth and development, Si is considered a beneficial element and is reported as being very useful to plants when they are under abiotic or biotic stress (Datnoff et al., 2001). An alleviating effect of Si on Al toxicity has been reported in many crops including soybean (Baylis et al., 1994), teosinte (Barcelo et al., 1993), sorghum (Hodson and Sangster, 1993), wheat, maize, cotton, and rice (Cocker et al., 1998).

Furthermore, the value of Si in this study was used to further estimate the rice yield. Therefore, calibration of soil test Si to relative yield (RY) by Narayanaswamy and Prakash (2009) was used as a reference to estimate the rice yield could be obtained from this study. Narayanaswamy and Prakash (2009) established three categories for the soil test- low (L), medium (M), and high (H). The high (RY > 95%) category was any soil tested above 65.0 mg L⁻¹. The medium (RY 75-95 %) and low (RY < 75%) zone corresponded to soils with Si content between 43.0 to 65.0 mg L⁻¹ and 0 to 43.0 mg L⁻¹. From this study, Si content in the soil at 30D and 60D was considerable in low category while at 90D was medium except CS1 and 120D, it was in the high zone.

4.4.5 Soil changes for untreated soil

A prolonged incubation of untreated soil with calcium silicate might have also influenced the changes in soil chemical characteristics. As such, CS0 (untreated soil) showed an increase in soil pH from 2.90 (prior to incubation) to 3.63 at 30D. A decrease in soil pH values was noted for 60D and 90D, likely due to pyrite oxidation in the soil system, and no significant effect was observed among the days of incubation. Meanwhile, exchangeable Al decreased significantly with increasing incubation time. For the first 2 months (30D and 60D), exchangeable Al was above the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$ and no significant difference between 30D and 60D was observed. Exchangeable Al was significantly reduced to $1.89 \text{ cmol}_c \text{ kg}^{-1}$ at 90D, but no significant effect was observed thereafter, i.e., at 120D. No significant effect on Si content was observed between 30D and 60D or between 90D and 120D. The Si content of the soil increased significantly, to 59.81 mg kg^{-1} , after 90D. The significant increase in Si was due to the hydrolysis of silicate minerals present in the acidic soils. For instance, the hydrolysis of silicate is generalized in the following reaction:



In this reaction, the base cation would commonly be Mg^{2+} or Ca^{2+} , H_2CO_3 is a proton source, HCO_3^- is bicarbonate, H_4SiO_4 is silicic acid, and gibbsite $[\text{Al}(\text{OH})_3]$ is a representative accessory mineral (Essington, 2005).

4.5 Conclusion

Application of calcium silicate showed an ameliorative effect on acidic soil, i.e., significant increase in soil pH, exchangeable Ca content, and Si content, and a reduction in exchangeable Al. This suggests that calcium silicate amendment is effective in alleviating Al toxicity in acidic, rice-cropped soils.

Chapter 5: Chemical characteristics of acidic sulfate soil as affected by addition of calcium silicate in-combination with and/or without ground magnesium limestone (GML) as soil amendments in a closed incubation system

5.1 Introduction

In Chapter 3 and Chapter 4, the effects of ground magnesium limestone (GML) and calcium silicate on acidic soil have been discussed as soil amendments, respectively. In those chapters, we showed that GML could to ameliorate soil acidity, improve soil pH and reduce Al/Fe toxicity, and that calcium silicate could alternatively ameliorate soil acidity while providing sufficient amount of Ca and Si.

In Chapter 5, the integral effect of both GML and calcium silicate on acidic soil is studied. Because both soil amendments have showed their primary effects on the soil in Chapter 3 and Chapter 4, and thus we can expect that their combination effects can be more beneficial in improving soil fertility. Namely, the combination of these two (2) soil amendments could be able to ameliorate the soil acidity, provide nutrient to plant and improve plant growth.

As mentioned in previous chapters, one of the widely used liming materials in Malaysia is GML, due to its local availability in Malaysia. No fixed rate of GML has been recorded for acidic soil, however, the common practice is 4 t ha⁻¹ for rice cultivation. Department of Agriculture, Ministry of Agriculture, Malaysia (2006) states GML application of 1.5-5 t ha⁻¹ based on soil acidity. Higher acidity soil requires more GML to neutralize the soil acidity and vice versa. Shazana et al. (2013) found that application of 4 t ha⁻¹ GML were able to improve the rice yield up to 4.2 t ha⁻¹ season⁻¹ in acidic sulfate soils of Kelantan. Besides that, application of GML in combination with organic matter (sugar cane-based organic fertilizer) produced rice yield at 7.5 t ha⁻¹ season⁻¹ (Suswanto et al., 2007).

GML is a good soil ameliorant, however, 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. And their constant application may have some limitations in its mobility. Soratto and Crusciol (2008) stated that, lime is not a very soluble materials and its dissociated components showed limited mobility, which at some point will restrict the correction effects (soil chemical characteristics) in topsoil under no soil tillage practice. Local farmers in Malaysia, often practice tillage with application of lime, yet GML solubility

is always an issue. For that reason, constant application of GML, season after season can be an ineffective practice. 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.

Because calcium silicate is chemically similar to carbonates (in GML) composition, it can be an alternative soil amendment on acidic soil. In addition, calcium silicate solubility is 6.78 times more soluble than lime (Alcarde and Rodella, 2003). Moreover, advantages of silicate compared to lime alone, are higher reaction rate and mobility down to deeper soil layers. With higher reaction rate, calcium silicate has the potential to solubilize and release more Ca in the available form for plant uptake. Besides that, silicate in the form of silicon (from calcium silicate dissolution) can strengthen crops against biotic and abiotic stresses on crops as globally reported in many studies (Peaslee and Frink, 1969; Menzies et al., 1992; Hodson and Frank, 1995; Romero-Aranda et al., 2006; Liang et al., 2007; Farnaz et al., 2012). (Chen et al., 2000; Gu et al., 2011) also reported that calcium silicate decreased the phytoavailability of Cd, Cu, Pb and Zn and eventually reduced the uptake of heavy metals in rice. Those means that the combination effects of GML and calcium silicate may have additional benefits to crop resistance and the environment.

Highly weathered soil such as Ultisol and Oxisol is often deficient in available Si because of its extensive leaching process (Crooks and Prentice, 2012). Therefore, application of silicate slag fertilizer (SSF), such as calcium silicate slag found to be effective in improving low soil-crop productivity. Datnoff et al. (1991) have clearly showed that calcium silicate was one of the silicon sources used in agriculture and its application to soil recorded positive effect for crop production.

This chapter aimed to evaluate the efficiency of calcium silicate with and/or without ground magnesium limestone (GML) application on soil chemical characteristics and to find the optimal recommendation rate of calcium silicate in combination with GML considering the positive effect of soil chemical characteristics on the acidic soil and the costs incurs.

5.2 Materials and Methods

5.2.1 Soil used in the study

Acidic soil was used in this study. The soil, classified as Typic Sulfaquepts, was collected from Merbok, Kedah, Peninsular Malaysia on January 1st, 2013. The soil sampling site was a rice-cropped area and the sampling was performed 1 month prior to rice cultivation (dry condition). A composite soil sample of approximately 100 kg was taken from topsoil (0-15 cm) depth using an auger for incubation. The sample was taken within a 0.5 ha region of the rice-cropped area. Samples for soil characterization were taken with a soil auger at five (5) different depths: 0-15, 15-30, 30-45, 45-60 and 60-75 cm depth (Table 3.1). After the soil sample collection, the samples were placed in plastic bags and transported back immediately to the Mineralogy Laboratory, Universiti Putra Malaysia for chemical characteristic analyses. Soil samples used for the submergence experiment were collected from the topsoil (0-15cm) samples. pH of the soil samples from all the sampling depths were lower than 3.5 which is the definition value for acid soil (Shamshuddin, 2006).

5.2.2 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) and ii) calcium silicate. These sources of soil amendments are easily and locally available in Malaysia. A factorial 4 x 4 experiments were arranged in a completely randomized design (CRD) with 3 replications.

Five hundred (500) grams of air-dried acidic soil, passed through 2 mm sieve was placed in a plastic pot. The soil samples were mixed with the soil amendments (Table 5.1) and inundated with water. The water level was maintained 5 cm from the soil surface throughout the experiment.

A general rate at 4 t ha⁻¹ GML was reported to be suitable to ameliorate acidic soils in Malaysia by Suswanto et al. (2007), Shazana et al. (2013). We also reached the same conclusion in Chapter 2. Meanwhile, the results of several field experiments suggest that, in general, 1.5-2.0 t ha⁻¹ calcium silicate slag may be adequate for lowland rice grown in Japan, Korea and Taiwan (Kono, 1969; Lian, 1976). In addition, the application rate of Si containing soil amendments (i.e calcium silicate) may depend on its chemical and physical factors plus soil factors (Savant et al., 1997).

Table 5.1**Soil treatments in combination of GML with calcium silicate**

Factor 1	GML rate at 0, 2, 4, 6 t ha ⁻¹
Factor 2	Calcium silicate rate at 0, 1, 2, 3 t ha ⁻¹

5.2.3 Soil and water analyses

The soil incubation was started on January 13th 2013 in an air-conditioned glasshouse where the temperature was approximately 30°C to 35°C. Soil submergence experiment was conducted for a total of 120 days. 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). Days of incubation, 30 (30D), 60 (60D), 90 (90D) and 120 (120D) days 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) with 10 g of air-dried soil and 25 mL of deionized water in a 100 mL plastic vial, capped and followed by 30 minutes shaking at 150 rpm. Soil pH were recorded using pH meter (PHM 93 Radiometer) after 1 hour; (ii) determination of exchangeable Al were done using 5 g of air-dried soil, extracted with 50 mL of 1 M KCl and the extracted mixture were shaken for 30 minutes, filtered using filter paper (Whatman No. 42) and subjected for exchangeable Al determination by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES); (iii) extractable Fe, Cu, Zn and Mn were extracted using Double Dilute Acid method; with 0.05 M HCl in 0.0125 M H₂SO₄ 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 and determined using Atomic Absorption Spectrometry (AAS) instrument; (iv) exchangeable K, Ca, Mg, Na and Fe were extracted using 1 N NH₄Cl (Shamshuddin, 2006). Briefly, 2 g of air-dried soil were put in a 50 mL centrifuge tubes and added 20 mL 1 M NH₄Cl. After intermittent shaking for 2 hours, the tubes were centrifuged at 2500 rpm for 15 minutes. The supernatant were transferred and filtered with filter paper into plastic vials. The exchangeable K, Ca, Mg, Na and Fe in the extract were determined by ICP-OES; (v) CEC of the soil was determined by using K₂SO₄ to extract NH₄⁺ from the

soil. Ammonium (NH_4^+) ion (for CEC value) was determined by Auto Analyzer (AA). Ten (10) g of air-dried soil were extracted using 100 mL of 1 N of NH_4OAc , followed with 100 mL of 95% ethanol and discarded the ethanol, followed with 100 mL of 0.05 M K_2SO_4 . The final extraction contains exchangeable cations; (vi) meanwhile, Si was extracted using 0.01 M CaCl_2 proposed by Narayanaswamy and 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 analyzed for Si using ICP-OES and (vii) carbon, nitrogen and sulphur were determined using CNS Analyzer.

Water sample was collected from each experimental pot. After filtering the samples with filter paper, water pH was determined using a pH meter. The concentration of Al, Fe, Ca and Si were determined using ICP-OES.

5.2.4 Statistical analysis

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

5.3 Results

Figure 5.1 and Table 5.2 show the result of soil pH, exchangeable cations (Al, Ca, Mg) and Si content under the combination of 4 levels of calcium silicate (0, 1, 2 and 3) t ha⁻¹ and 4 levels of GML (0, 2, 4 and 6) t ha⁻¹. The means marked with the same letter for each calcium silicate levels are not significantly different at $p < 0.05$ (Tukey's Test).

5.3.1 Soil pH changes under different level of calcium silicate and GML

The require level of soil pH for rice growth is more than 4 as suggested by Shamshuddin (2006). 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 5.1a-d and Table 5.2. 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 while 4 t ha⁻¹ GML significantly increased the soil pH under 2 and 3 t ha⁻¹ of calcium silicate compared to the soil pH without GML and 2 t ha⁻¹ 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 while 2 t ha⁻¹ GML significantly increased the soil pH under 1 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. Meanwhile the soil with 4 t ha⁻¹ GML significantly increased the soil pH under 1 and 3 t ha⁻¹ calcium silicate compared to 0 and 2 t ha⁻¹ of GML.

5.3.2 Exchangeable aluminium (Al) and Al saturation changes in the soils under different level of calcium silicate and GML

Initially, the exchangeable Al and Al saturation were $5.18 \text{ cmol}_c \text{ kg}^{-1}$ and 49.95%, respectively. Those value above the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$ (Hiradate et al., 2007) and 30% (Dobermann and Fairhurst, 2000), respectively. The Aluminium (Al) toxicity of the acidic soil was reduced after the addition of the soil amendments corresponding with the incubation period. Both the reduction in the exchangeable Al (Figure 5.1e-h and Table 5.2) and the Al saturation (Figure 5.1 i-l and Table 5.2) were both significant as the soil amendments rates on the acidic soil increased. As the soil pH increased, the exchangeable Al decreased (Figure 5.4), and this marks the beneficial effect of combined soil amendments.

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. We observed that the exchangeable Al for all the treated soils were below the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$ (Hiradate et al., 2007) at 90D and 120D. The soil without GML significantly increased the exchangeable Al under 0, 2 and 3 t ha^{-1} of calcium silicate compared to 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. It gradually decreased with the incubation period.

Table 5.2

Effect of calcium silicate (CS) and/or ground magnesium limestone (GML) application on soil chemical properties. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey's Test)

Days	CS	GML	pH _{H2O}	Al	Ca	Mg	Si
			(1:2.5)	Exchangeable cations (cmol _c kg ⁻¹)		mg kg ⁻¹	
30	0	0	3.63 ^b	3.34 ^a	2.41 ^c	3.13 ^c	30.65 ^a
		2	3.97 ^a	1.92 ^b	3.73 ^b	3.79 ^b	29.48 ^{ab}
		4	3.98 ^a	1.64 ^b	4.13 ^b	4.16 ^b	23.80 ^b
		6	4.26 ^a	0.65 ^c	5.08 ^a	4.84 ^a	26.50 ^{ab}
	1	0	3.62 ^d	2.91 ^a	3.06 ^d	2.99 ^c	29.90 ^b
		2	3.88 ^c	2.24 ^a	4.05 ^c	4.15 ^b	33.02 ^{ab}
		4	4.09 ^b	1.18 ^b	4.72 ^b	4.59 ^b	33.73 ^{ab}
		6	4.34 ^a	0.46 ^b	5.78 ^a	5.22 ^a	37.13 ^a
	2	0	3.77 ^d	2.36 ^a	3.75 ^d	3.15 ^c	40.84 ^a
		2	3.98 ^c	1.44 ^b	4.53 ^c	4.09 ^b	43.80 ^a
		4	4.18 ^b	0.83 ^c	5.5 ^b	4.57 ^{ab}	38.09 ^a
		6	4.40 ^a	0.38 ^d	6.12 ^d	4.94 ^a	38.08 ^a
	3	0	3.75 ^d	2.14 ^a	4.19 ^c	3.41 ^c	44.82 ^{ab}
		2	4.03 ^c	1.20 ^b	5.26 ^b	4.13 ^b	51.79 ^a
		4	4.30 ^b	0.64 ^c	6.44 ^a	5.03 ^a	50.12 ^{ab}
		6	4.53 ^a	0.20 ^d	6.90 ^a	5.21 ^a	43.21 ^b

Days	CS	GML	pH _{H2O}	Al	Ca	Mg	Si
			(1:2.5)	Exchangeable cations (cmol _c kg ⁻¹)		mg kg ⁻¹	
60	0	0	3.71 ^d	2.77 ^a	2.48 ^d	3.14 ^d	24.90 ^a
		2	4.06 ^c	1.62 ^b	3.30 ^c	3.57 ^c	24.20 ^a
		4	4.31 ^b	0.79 ^c	4.16 ^b	4.23 ^b	24.50 ^a
		6	4.49 ^a	0.36 ^c	5.03 ^a	4.78 ^a	22.20 ^a
	1	0	3.84 ^b	2.88 ^a	2.80 ^c	2.57 ^d	16.46 ^b
		2	3.83 ^b	1.92 ^b	4.60 ^b	3.58 ^c	17.87 ^b
		4	4.08 ^{ab}	1.45 ^b	5.79 ^a	4.65 ^b	22.20 ^{ab}
		6	4.39 ^a	0.66 ^c	6.84 ^a	5.35 ^a	30.30 ^a
	2	0	3.63 ^c	2.12 ^a	4.06 ^d	3.05 ^d	33.06 ^a
		2	3.80 ^c	1.26 ^b	5.16 ^c	3.83 ^c	33.81 ^a
		4	4.09 ^b	0.61 ^c	6.17 ^b	4.49 ^b	36.22 ^a
		6	4.36 ^a	0.22 ^d	7.35 ^a	5.13 ^a	30.01 ^a
	3	0	3.66 ^b	2.03 ^a	4.75 ^d	3.20 ^c	40.81 ^a
		2	3.91 ^b	1.36 ^{ab}	5.78 ^c	4.01 ^b	36.71 ^{ab}
		4	4.30 ^a	0.38 ^{bc}	6.95 ^b	4.63 ^b	36.89 ^{ab}
		6	4.55 ^a	0.14 ^c	8.40 ^a	5.36 ^a	33.58 ^b

Days	CS	GML	pH _{H2O} (1:2.5)	Al Exchangeable cations (cmol _c kg ⁻¹)	Ca	Mg	Si mg kg ⁻¹
90	0	0	3.40 ^b	1.35 ^a	1.68 ^b	1.79 ^a	59.80 ^a
		2	3.63 ^b	0.64 ^b	1.83 ^b	1.76 ^a	62.95 ^a
		4	3.81 ^{ab}	0.36 ^b	2.33 ^{ab}	2.03 ^a	66.36 ^a
		6	4.08 ^a	0.12 ^b	2.91 ^a	2.35 ^a	74.13 ^a
	1	0	3.49 ^c	0.85 ^a	1.87 ^d	1.48 ^d	83.53 ^a
		2	3.76 ^b	0.84 ^a	4.23 ^c	3.30 ^c	83.62 ^a
		4	3.89 ^b	0.47 ^b	5.24 ^b	3.95 ^b	92.04 ^a
		6	4.13 ^a	0.16 ^c	6.53 ^a	4.72 ^a	96.86 ^a
	2	0	3.62 ^b	1.25 ^a	4.00 ^c	2.68 ^c	55.35 ^a
		2	3.49 ^b	0.89 ^b	4.93 ^b	3.54 ^b	55.58 ^a
		4	3.79 ^b	0.39 ^c	6.13 ^a	4.31 ^a	79.74 ^a
		6	4.19 ^a	0.14 ^d	6.98 ^a	4.85 ^a	60.33 ^a
	3	0	3.84 ^b	1.00 ^a	4.27 ^c	2.67 ^c	65.10 ^{ab}
		2	4.12 ^{ab}	0.46 ^b	6.04 ^b	3.97 ^b	69.08 ^a
		4	4.16 ^{ab}	0.46 ^b	6.02 ^b	4.01 ^b	53.16 ^b
		6	4.52 ^a	0.08 ^b	7.69 ^a	4.95 ^a	76.87 ^a

Days	CS	GML	pH _{H2O}	Al	Ca	Mg	Si
			(1:2.5)	Exchangeable cations (cmol _c kg ⁻¹)		mg kg ⁻¹	
120	0	0	3.65 ^d	1.90 ^a	3.03 ^c	3.05 ^c	72.78 ^{ab}
		2	3.85 ^c	0.98 ^b	3.95 ^b	3.65 ^{bc}	52.06 ^b
		4	4.03 ^b	0.57 ^{bc}	4.58 ^b	4.10 ^b	74.40 ^{ab}
		6	4.42 ^a	0.13 ^c	6.24 ^a	5.19 ^a	79.36 ^a
	1	0	3.71 ^b	1.50 ^a	3.32 ^c	2.89 ^c	77.25 ^a
		2	3.96 ^b	0.69 ^b	4.54 ^b	3.70 ^b	81.52 ^a
		4	4.28 ^a	0.27 ^c	5.10 ^b	4.10 ^b	96.33 ^a
		6	4.44 ^a	0.14 ^c	6.24 ^a	4.77 ^a	82.91 ^a
	2	0	3.77 ^c	1.24 ^a	4.60 ^d	3.36 ^c	77.75 ^a
		2	3.99 ^{bc}	0.68 ^b	5.53 ^c	3.89 ^c	99.02 ^a
		4	4.29 ^b	0.35 ^{bc}	6.63 ^b	4.79 ^b	88.05 ^a
		6	4.64 ^a	0.09 ^c	7.74 ^a	5.52 ^a	90.72 ^a
	3	0	3.95 ^b	1.12 ^a	4.94 ^c	3.04 ^d	81.71 ^a
		2	4.12 ^b	0.57 ^b	6.07 ^b	3.86 ^c	75.67 ^a
		4	4.51 ^a	0.16 ^c	6.52 ^b	4.29 ^b	76.72 ^a
		6	4.51 ^a	0.06 ^c	7.98 ^a	4.88 ^a	89.90 ^a

5.3.3 Exchangeable calcium (Ca) and magnesium (Mg) changes in the soils under different level of calcium silicate and GML

Require levels of exchangeable Ca and Mg for rice growth are 2 cmol_c kg⁻¹ (Palhares de Melo et al., 2001) and 1 cmol_c kg⁻¹ (Dobermann and Fairhurst, 2000), respectively. The soil treated with calcium silicate and GML recorded increase of exchangeable Ca and Mg in the soil. Figure 5.1m-p and Table 5.2 show 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 different rate (0, 1, 2, 3 t ha⁻¹) of calcium silicate addition at 30D, 90D and 120D, respectively. On the other hand, the exchangeable Mg (Figure 5.1 q-t and Table 5.2) 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.

5.3.4 Si content changes in the soils under different level of GML and calcium silicate

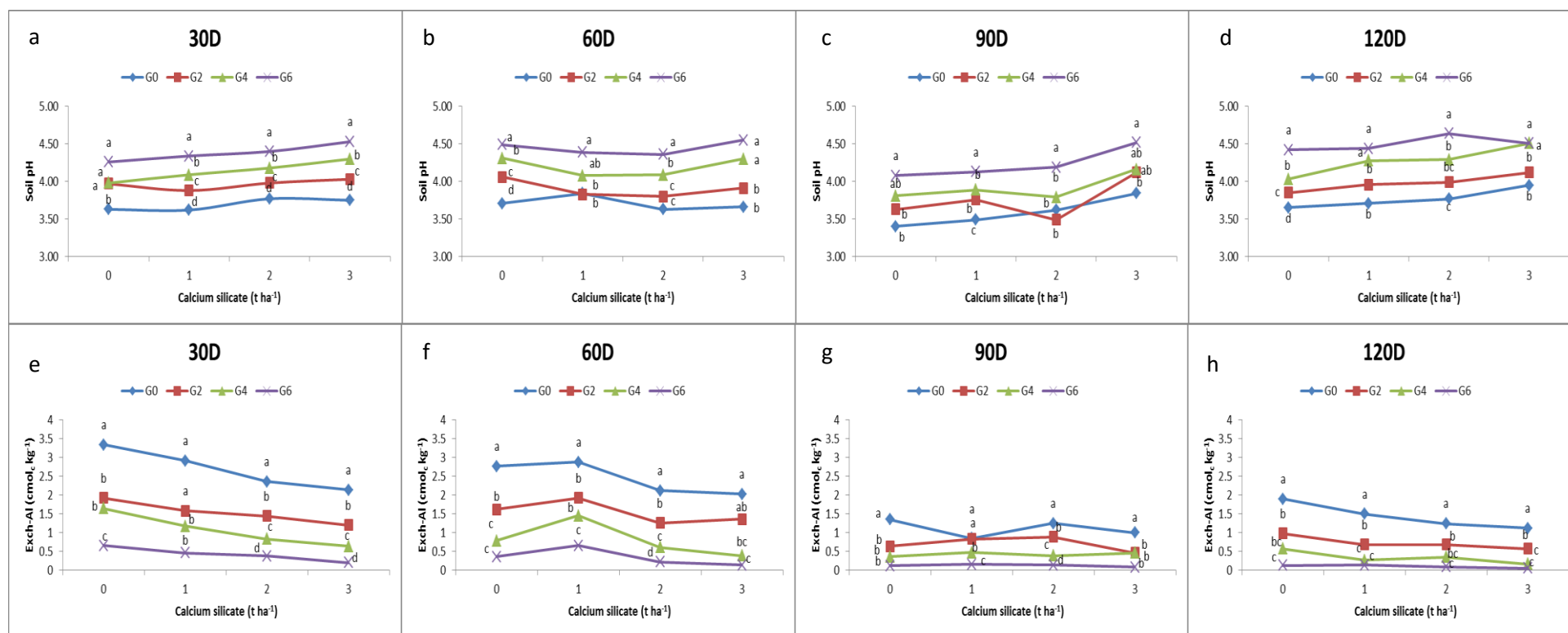
Required Si level for rice growth is at least 43 mg kg⁻¹, as suggested by Narayanaswamy and Prakash (2009). In this study, the initial Si value was 25.8 mg kg⁻¹ in the soils. Table 5.3 shows the Si value ranges of each incubation day summarized based on Table 5.2 The increment of the Si values were clearly marked with the increase in the days of incubation. A sigmoid (s-curve) increment trend was noted.

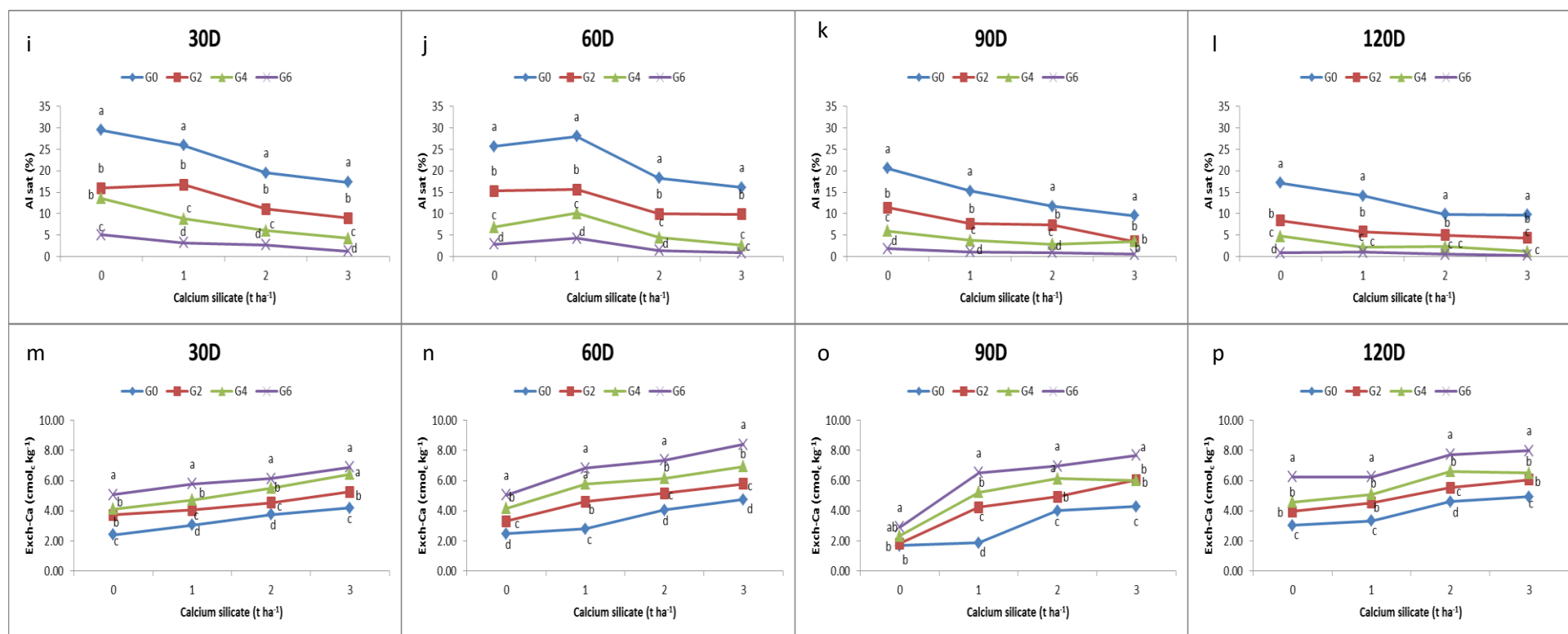
Table 5.3

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

In both reproductive and flowering stages, the Si content ranges were higher than 40 mg kg^{-1} under any combinations of the soil amendments while a combination levels (3 t ha^{-1} calcium silicate) achieved the value in the vegetative stage. The result indicates the soil amendment (calcium silicate) has potential to release sufficient Si to the soil for plant uptake at least at 60th day. The released Si is expecting to be in the available form, and this form complement well with the crop requirements.





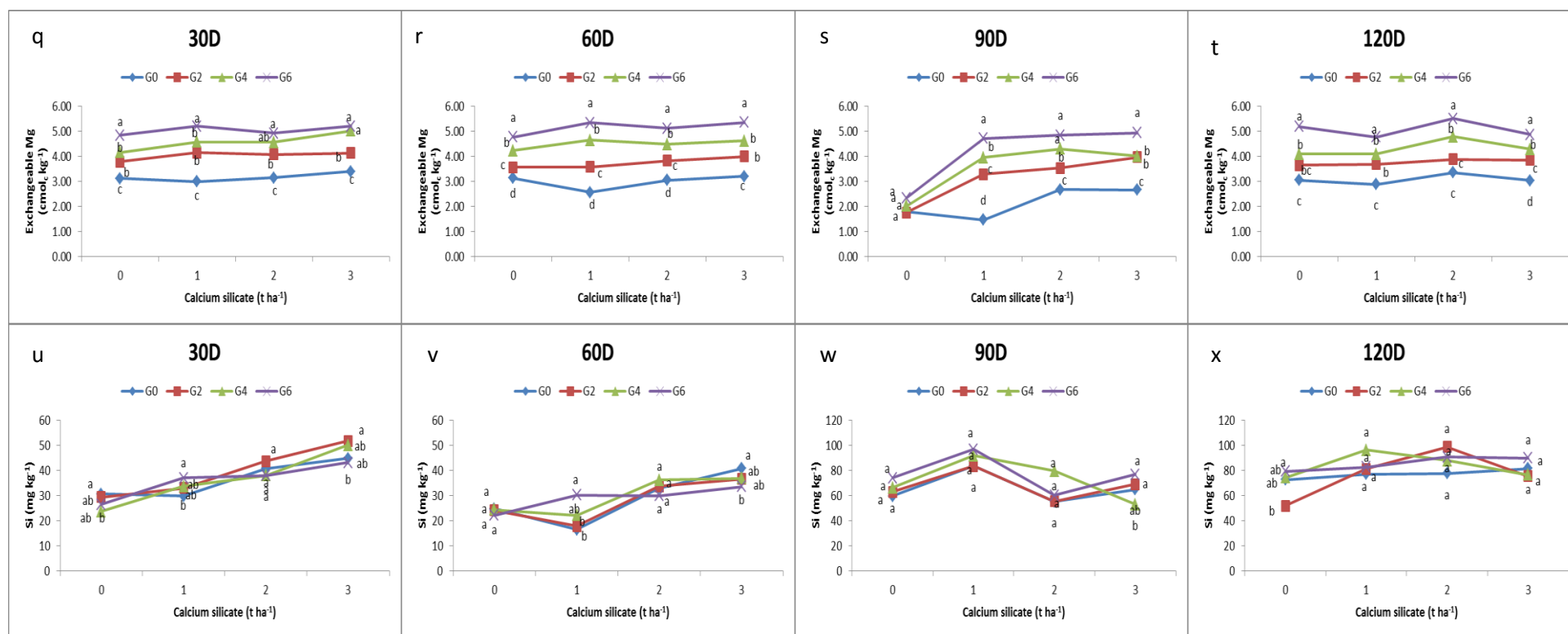
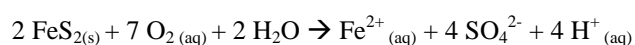


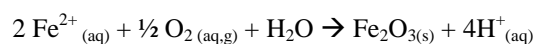
Figure 5.1 Selected soil chemical properties as an indicator of ameliorative effects under different rate of calcium silicate incorporated with GML (soil amendments) on acidic soil of rice-cropped soil. Means marked with the same letter for each calcium silicate treatments are not significantly different 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)

5.3.5 Soil acidity reduction with time

Figure 5.2 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 show that the lines at 60D, 90D and 120D were shifted to the left. The line shift to the left indicate 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 oxidized during the incubation period. The oxidation of pyrite, which produces acidity, may have taken place according to the following reactions outlined by van Breeman (1976):



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



The results from the current study are consistent with those from other studies of acidic soils (Shamshuddin and Auxtero, 1991; Shamshuddin et al., 1995; Shamshuddin et al., 2014). Furthermore, Shamshuddin et al. (2004) reported that soil pH in the Cg horizon (subsoil) was lowered by 1 unit after 12 weeks of incubation, indicating the continuous ameliorative effects of soil amendments at subsoil level. The root of rice crop may reach subsoil at later growth stages of more than 60 days after planting/ seed broadcasting.

The soil pH (Figure 5.2) did not exceed pH 5 compared to the water solution pH as shown in Figure 5.3. At 30D (Figure 5.3a), Al_{water} concentration decreased with the increment in the water solution pH. The Al_{water} concentration was observed to gradually increase at 60D (Figure 5.3b), 90D (Figure 5.3c) and 120D (5.3d). Their gradual improvement will support positive crop growth inline with vegetative, productive, flowering and maturity stages; a.k.a paddy growth stages.

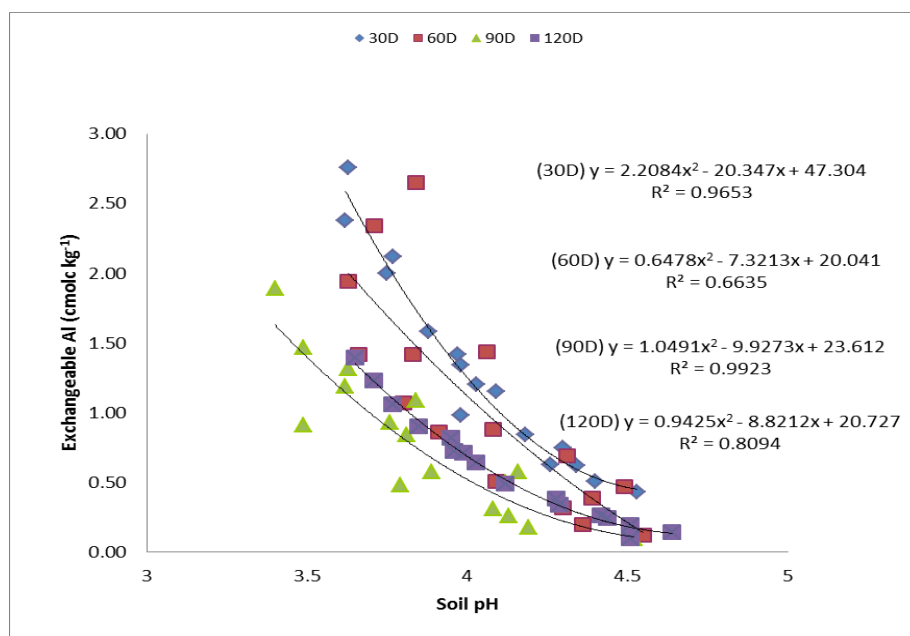


Figure 5.2 Relationship between exchangeable Al against soil pH on acidic sulfate soil. Polynomial regressions were conducted for the curves

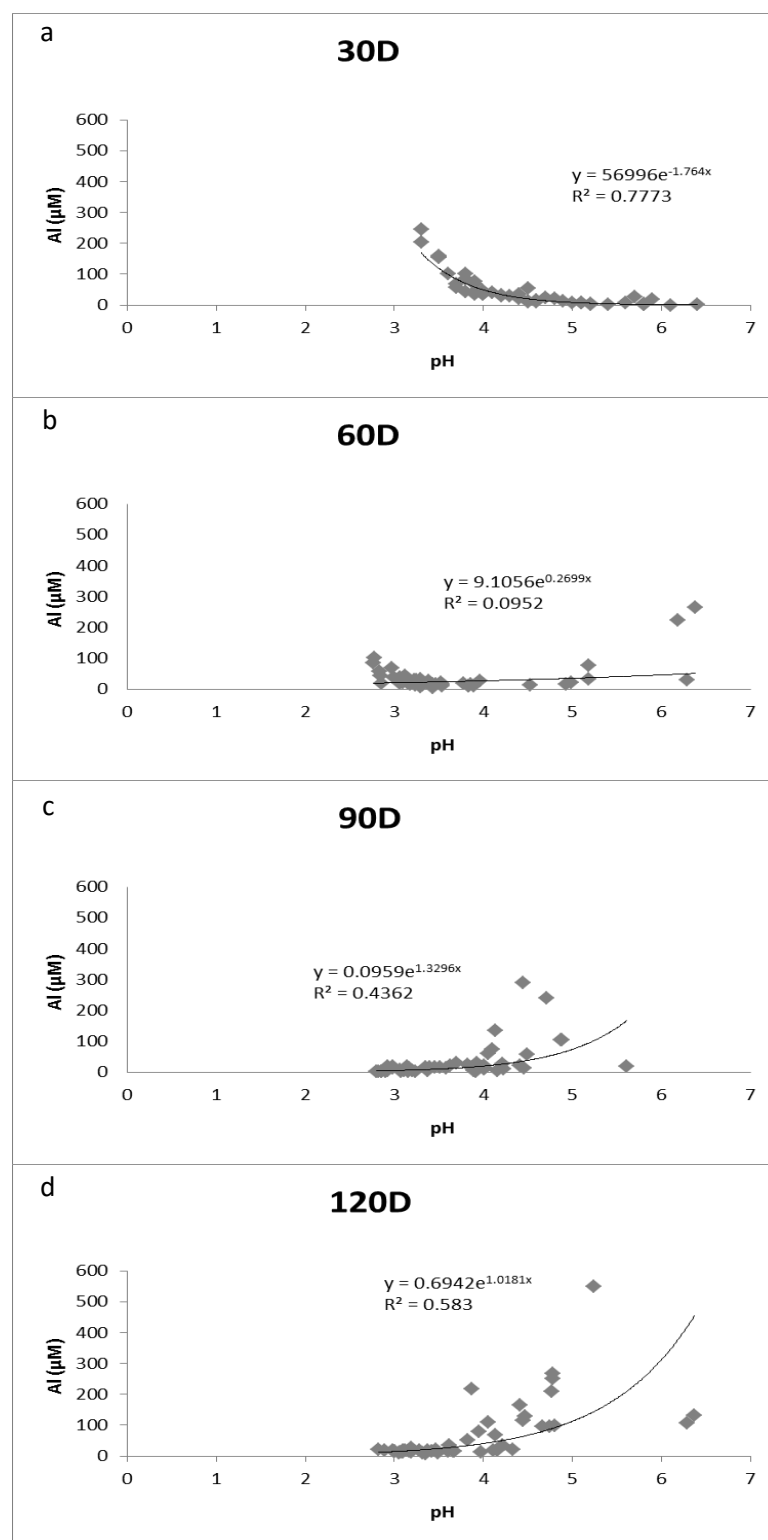


Figure 5.3 Relationship between Al_{water} concentration and pH of water solution after 30 (a), 60 (b), 90 (d) and 120 (d) incubation period

5.4 Discussion

In this chapter, we examined the effect of the combination of calcium silicate and GML on the improvement of acidic soil 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 (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 and Fairhurst, 2000)
- v) Si content > 43 mg kg⁻¹ (Narayaswamy and Prakash, 2009)

In this section, we first discuss about 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 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 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) 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 5.2) and water (Figure 5.3). This will support positive crop growth inline with vegetative, reproductive and flowering of rice growth phases. Second, it is more practical and applicable by the local farmers compared to 60D, 90D or 120D because 30D 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.

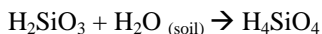
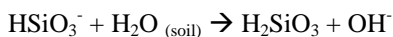
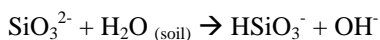
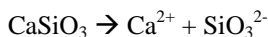
Because farmers are currently using GML at rate at 4 t ha⁻¹ which costs approximately USD 668, we seek for the optimal combinations of calcium silicate and GML to reduce the cost.

5.4.1 GML and calcium silicate combined ameliorative effects on the selected soil characteristics

1. Calcium silicate ameliorative effect mechanism and theory

Studies conducted by Haak and Siman (1992) and Myhr and Erstad (1996) showed Si could effectively reduce Al toxicity. Calcium silicate is a source of silicon to the soil and plants. In this study, 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 soil for crop production and other means.

Acidic soils are known to be high acidity (pH 2.5-3.5), and this is a major limitations for nutrient uptake and crop growth. In order to alleviate this issue, some soil amendments are required. One potential soil amendment is calcium silicate slag that contains significant amount of calcium and silicon. However, their exact mechanism still remains as theory. Several authors have postulated their mechanism (Nolla et al., 2013; Alcarde and Rodella, 2003) as shown below:



Acidity in soils comes from H^+ and Al^{3+} ions in the soil solution and adsorbed to soil surfaces. While pH is the measure of H^+ in solution, Al^{3+} is important in acid soils because between pH 4 and 6, Al^{3+} reacts with water (H_2O) forming AlOH^{2+} , and $\text{Al}(\text{OH})_2^+$, releasing extra H^+ ions. Every Al^{3+} ion can create 3 H^+ ions. Many other processes contribute to the formation of acid soils including rainfall, fertilizer use, plant root activity and the weathering of primary and secondary soil minerals. Acid soils can also be caused by pollutants such as acid rain and mines spoiling. (https://en.wikipedia.org/wiki/Soil_pH-retrieved 03 May 2016).

Under Merbok (Kedah) acidic soil condition, soil acidity is more prevalent. Al (III) which is Al^{3+} potentially released from dissociation of gibbsite, $\text{Al}(\text{OH})_3$, under Malaysia highly weathered tropical soils. Acidic soils under study have significant amount of Al in the soil system. Thus, acid soil may give rise to extra H^+ in the soil system, and increase the soil acidity. Application of calcium silicate in-combination with GML may reduce the soil acidity in this acidic soil area.

It is a general understanding that, the source of acidity in soils is due to increase in hydrogen (H^+) ions concentration in the soil exchange sites. One way to reduce the acidity is by reducing the capability of H^+ to fill-in the soil exchange sites. With 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). 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 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 $\text{Ca}(\text{OH})_2$ in the soil system. When necessary, they can dissociate and supply Ca^{2+} to the soil. This will give continual liming effect to the acidic soils, plus calcium is a macronutrient for paddy crop. And also, these free hydroxyl ions may bind Al^{3+} to form inert Al-hydroxides (neutralize 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.

Besides that, several other mechanisms have been postulated in reducing Al toxicity by Si-rich materials. Cations such as Al^{3+} levels can be both decreased by increasing pH (Carvalho-Pupatto et al., 2004) or by reactions with Si and later precipitation as hydroxylaluminosilicate, which reduces its availability noted by Exley (1998).

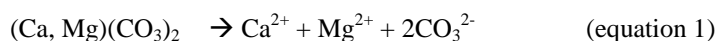
All in all, it is possible to postulate five different mechanism of Al toxicity reduction by Si-rich compounds. Firstly, monosilicic acids can increase soil pH (Lindsay, 1979). Secondly, monosilicic acids can be adsorbed on aluminium hydroxides, impairing their mobility (Panov et al., 1982). Thirdly, soluble monosilicic acid can form slightly soluble substances with ions of Al (Lumdson and Farmer, 1995). Another possibility for Al toxicity reduction by Si-rich compounds can be strong adsorption of mobile Al on silica surfaces (Schulthess and Tokunda, 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.

Ma and Matsumoto (1997) found that silicic acid addition decreased Al inhibition effect on corn root growth with the presence of Al in soil solution. 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. Further, Cocker et al (1998), believes that the interaction between aluminium and silicon can also occur inside the plant.

2. GML ameliorative effects mechanism

GML is well known to increase the soil pH, and release (add) Ca and Mg into the soil system.

GML ameliorative reactions are shown below:



GML dissolves gradually within 14 days of its application 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 neutralize Al by forming inert Al-hydroxides (equation 3). Combination of calcium silicate and GML, both shows 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.

3. Calcium silicate (slag) potential as soil amendments and/or fertilizers

Slags (or calcium silicate) used in agriculture release calcium, magnesium and silicate (SiO_3^{-2}) ions in the soil solution, and have the same valence as the carbonate (CO_3^{-2}) from limestone. Thus, calcium silicate has the similar potential to reduce soil acidity than limestone. Moreover, calcium silicate contain substantial amount of silica and can be used as a nutrient source for plants.

Application of slag has shown positive effect in agriculture as it increased the crop yield such as sorghum (Ribeiro et al., 1986), potato (Wutke et al., 1962), soybean (Dalto, 2003) and corn (Uitdewilligen, 2004). The authors attributed that application of slag were able to neutralize Al^{3+} in soil solution and have same efficiency to limestone in increment of soil pH.

Several factors influence on the sustainability of slag and/or limestone such as climate, soil management, particle size and time of the amendments in the soil (Alcarde and Rodella, 2003). Residual effect of slag could sustain several years for rice crop field, thus reduce the cost of their re-application (Lian, 1992). In other hand, Prado et al. (2003) observed that slag sustained its residual effect for about 56 months for sugarcane.

5.4.2 Relationship between soil pH and exchangeable Al at 30 days of incubation

Figure 5.4 shows relationship between soil pH and exchangeable Al at the 30th day of the incubation. The result clearly shows that exchangeable Al decreased with increment in soil pH. However, the addition of calcium silicate alone could not make the exchangeable Al value in the soil lower than the critical value ($< 2 \text{ cmol}_c \text{ kg}^{-1}$) and soil pH higher than 4 to avoid their inhibitory effects on rice growth. The distribution pattern shifted to the right when soil was treated with both GML and calcium silicate, indicating the combined ameliorative effects of both soil amendments. Under the most of the combinations of both amendments with different application levels, the exchangeable Al and soil pH values falls within the critical values ($\text{Al} < 2 \text{ cmol}_c \text{ kg}^{-1}$ and $\text{soil pH} > 4$). Thus, the result indicates that addition of both soil amendments improved the acidic soil compared to single soil amendment application.

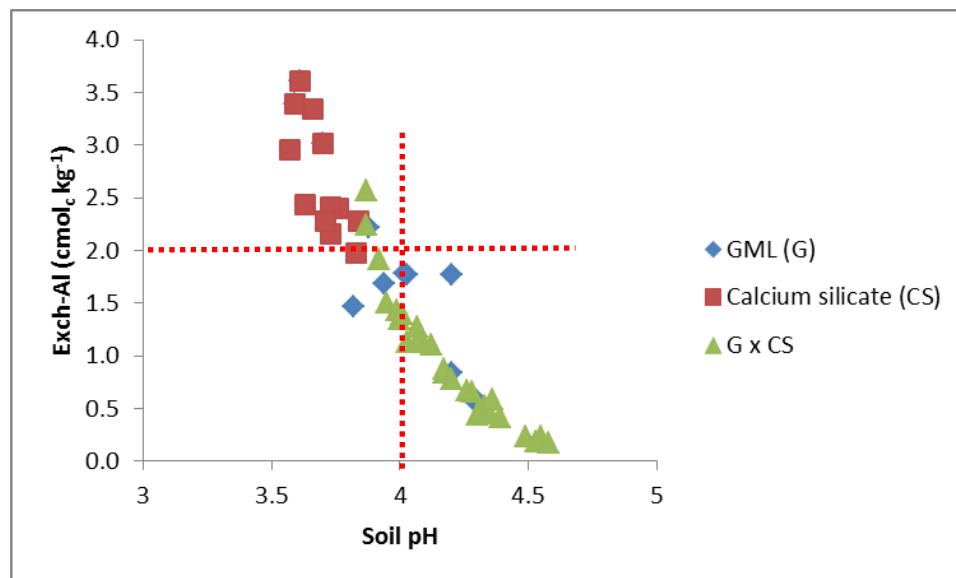


Figure 5.4 Relationship between exchangeable Al and soil pH at the 30th day of the incubation

5.4.3 Relationship between silicon content and aluminium at 30 days of incubation

Figure 5.5 shows the relationship between exchangeable Al and Si content at the 30th day of the incubation. 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 $\text{cmol}_c \text{ kg}^{-1}$. The Si content was lower than sufficient level ($> 43 \text{ mg kg}^{-1}$) (Narayaswamy and Prakash, 2009) for crop growth only with GML though the exchangeable Al is lower than the critical value. The combinations of GML and calcium silicate as soil amendments on acidic soil performed well for both exchangeable Al ($< 2 \text{ cmol}_c \text{ kg}^{-1}$) and Si ($> 43 \text{ mg kg}^{-1}$) values compared to application of GML or calcium silicate only. Under proper combination of application levels of the both of the amendments, exchangeable Al were lower than 2 $\text{cmol}_c \text{ kg}^{-1}$, while Si contents ranged between 40-50 mg kg^{-1} .

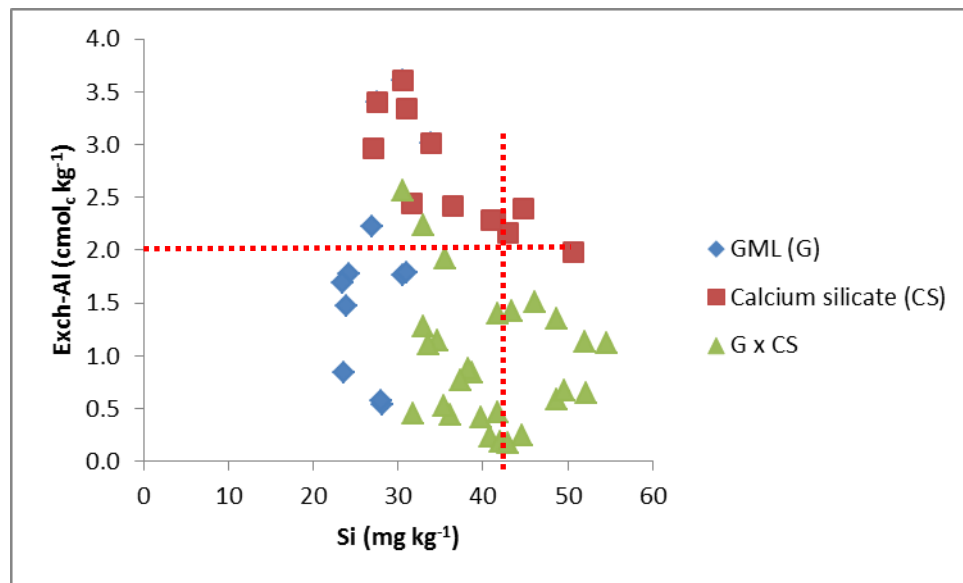


Figure 5.5 Relationship between exchangeable Al and Si content at the 30th day of the incubation

5.4.4 Relationship between soil pH and silicon content at 30 days of incubation

Figure 5.6 shows the relationship between soil pH and silicon content. Soil pH positively correlates with silicon content under the calcium silicate treatment alone. The application of one type of soil amendments alone, either GML or calcium silicate, was unable to positively ameliorate the soil condition to the recommended levels. Namely, none increased the soil pH above pH 4 and increased the silicon content above 43 mg kg⁻¹. Statistically, no significant relationships between soil pH and silicon content were observed for soil treated with 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 the above recommended levels.

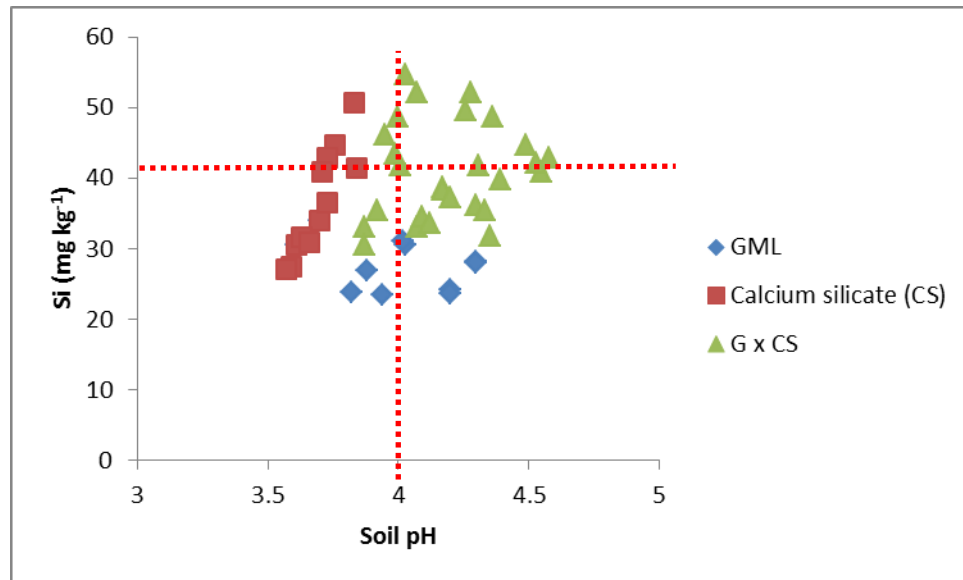


Figure 5.6 Relationship between Si and soil pH at the 30th day of the incubation

5.4.5 Relationship between exchangeable Ca and exchangeable Al at 30 days of incubation

Figure 5.7 shows the relationship between exchangeable Ca and exchangeable Al at the 30th days of the incubation. Exchangeable Ca negatively correlates with exchangeable Al. As the exchangeable Ca increased, the exchangeable Al decreased. Single or combine application of soil amendments made the exchangeable Ca reach the require of 2 $\text{cmol}_c \text{kg}^{-1}$ (Palhares de Melo et al., 2001). However, the application of calcium silicate alone did not reduced the exchangeable Al below critical level of 2 $\text{cmol}_c \text{kg}^{-1}$ (Hiradate et al., 2007) while the application of GML alone or exchangeable Al was reduced below critical level ($< 2 \text{ cmol}_c \text{kg}^{-1}$) for application of GML alone and the combination (GML with CS).

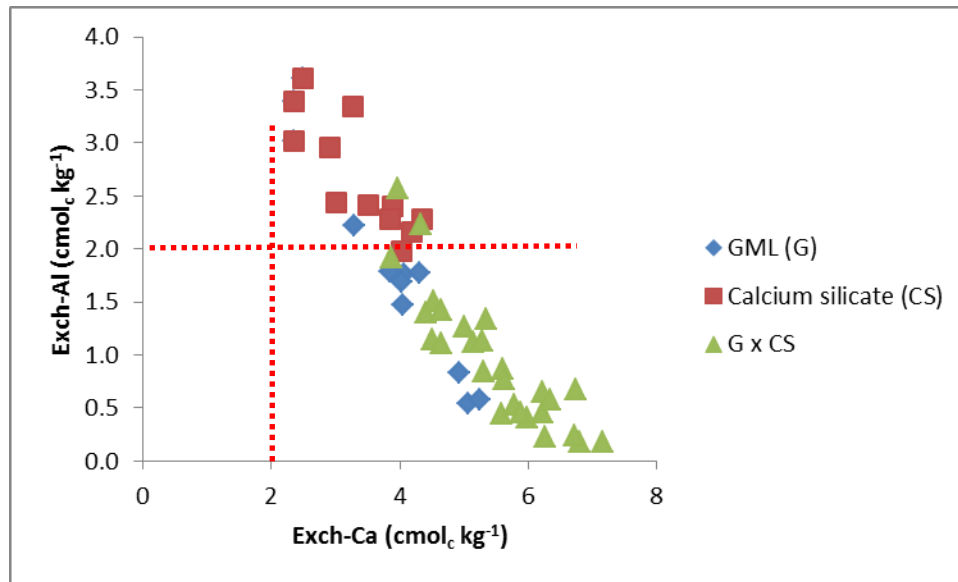


Figure 5.7 Relationship between exchangeable Al and exchangeable Ca at the 30th day of the incubation

5.4.6 Relationship between exchangeable Mg and exchangeable Al at 30 days of incubation

Figure 5.8 shows on the relationship between exchangeable Mg and exchangeable Al at 30 days of incubation. It shows that as the exchangeable Mg increased, the exchangeable Al decreased. The addition of calcium silicate alone did not decreased the exchangeable Al below the critical level of $2 \text{ cmol}_c \text{ kg}^{-1}$. 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 $2 \text{ cmol}_c \text{ kg}^{-1}$. The application of the soil amendments alone or with the combination, increased in exchangeable Mg above the require level of $1 \text{ cmol}_c \text{ kg}^{-1}$.

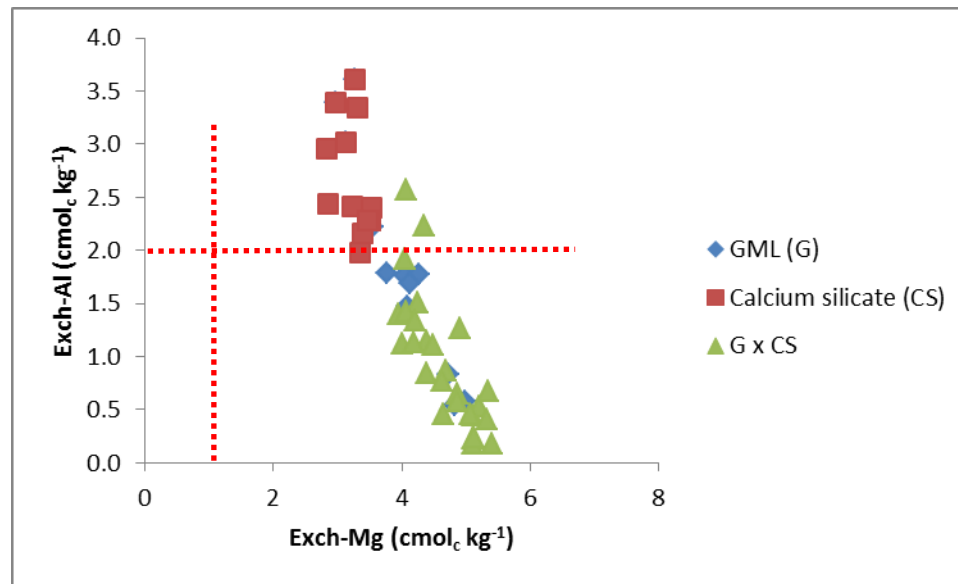


Figure 5.8 Relationship between exchangeable Al and exchangeable Mg at the 30th day of the incubation

5.4.7 Effective combination rate of calcium silicate and GML as soil amendments

The effective rates of the combinations were evaluated based on the effect at 30th of the incubation, considering the guideline for soil chemical characteristics to achieve good rice growth suggested by past studies. The following are such values used in this study.

- a) Soil pH > 4 (Shamshuddin, 2006)
- b) Exchangeable Al < 2 cmol_c kg⁻¹ (Hiradate et al., 2007)
- c) Exchangeable Ca > 2 cmol_c kg⁻¹ (Palhares de Melo et al., 2001)
- d) Exchangeable Mg > 1 cmol_c kg⁻¹ (Dobermann and Fairhurst, 2000)
- e) Si content > 43 mg kg⁻¹ (Narayanaswamy and Prakash, 2009)

For soil pH (Table 5.4) and exchangeable Al (Table 5.5), the combination rate in yellow color achieved the recommended level of more than 4 and less than 2 cmol_c kg⁻¹, respectively. On the other hand, all the combination rate reached the recommended level (yellow color) of 2 cmol_c kg⁻¹ and 1 cmol_c kg⁻¹ for exchangeable Ca (Table 5.6) and Mg (Table 5.7), respectively. Furthermore, for Si content (Table 5.8), the combination in yellow color achieved the recommended level of more than 40 mg kg⁻¹. Finally, Table 5.9 shows the soil chemical characteristics which meet the recommended level for each combination of calcium silicate and GML. It show that, combination of 3 t ha⁻¹ calcium silicate with 2, 4 or 6 t ha⁻¹ GML achieved the recommended levels for all the 5 soil chemical characteristics of, the soil pH, exchangeable Al, Ca, Mg and Si content (marked in green color). 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 color), 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 combination 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 achived 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 40 mg kg⁻¹. The remaining combination rate of calcium silicate and GML achieved 3 or less of 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 analyzed for the feasibility analysis to find out most optimal combination balancing the the fertility improvement and the cost-effectiveness.

Table 5.4

Effect of calcium silicate in-combination with GML on soil pH at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey`s Test)

	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

Table 5.5

Effect of calcium silicate in-combination with GML on exchangeable Al at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey's Test)

	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
6	0.65 ^c	0.46 ^b	0.38 ^d	0.20 ^d

Table 5.6

Effect of calcium silicate in-combination with GML on exchangeable Ca at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey's Test)

	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

Table 5.7

Effect of calcium silicate in-combination with GML on exchangeable Mg at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey's Test)

	Calcium silicate (t ha ⁻¹)			
GML (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

Table 5.8

Effect of calcium silicate in-combination with GML on Si content at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey's Test)

	Calcium silicate (t ha ⁻¹)			
GML (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 5.9

Combination of calcium silicate with GML achieve the recommended value of soil chemical characteristics

	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

5.4.8 Feasibility analysis

Table 5.10 shows the cost incurs for soil amendments application. The cost includes the price of soil amendments and labor cost. Currently, the price for both calcium silicate slag and GML are USD 30 t⁻¹ and USD 122 t⁻¹, respectively while the labor 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 color). Therefore, the total cost less than USD 668 was considered. From the Table 5.9, it shows that 9 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 (marked in yellow color).

Out of the possible 2 recommendations, the combination of 3 t ha⁻¹ calcium silicate with 2 t ha⁻¹ GML achieved the recommendation 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 achieved the pH level at 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 the this recommendation is USD 184 more beneficial per ha (28%) for the farmers. In this study, the pH level under the common practice with 4 t ha⁻¹ of GML was also 3.98 (Table 5.4) 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 40 mg kg⁻¹ (Table 5.8), indicating that the combination of 2 t ha⁻¹ calcium silicate with 2 t ha⁻¹ GML may improve rice growth better than the common practice in addition to the cost reduction of USD 184. Therefore, the combination can be advantageous for the farmers in spite of the pH level.

Both of the recommendation are more beneficial than the common 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 compensate 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 recommendation 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

Table 5.10**Cost incurs for application of soil amendments**

	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****5.5 Conclusion**

The possible recommendation rate are 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. Those 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.

Chapter 6 Efficacy of calcium silicate on greenhouse gases emissions of rice-cropped soil

6.1 Introduction

In Chapter 4, the effect of calcium silicate on acidic sulfate soil has been discussed. In that chapter, we showed that calcium silicate could be an alternative soil amendment as it could ameliorate soil acidity while providing sufficient amount of Ca and Si. On the other hand, in Chapter 5, the effect of calcium silicate in combination with ground magnesium limestone (GML) has been discussed. In that chapter, we assessed the integral effect of both soil amendments calcium silicate and GML on acidic sulfate soil. In addition 5, we also identified the optimal combinations ameliorate soil acidity and improve soil fertility of acidic sulfate soil. From those Chapters 4 and 5, addition of calcium silicate showed the positive effect in reducing soil acidity and improving soil fertility of acidic sulfate soil in Malaysia. Besides the positive effect on the soils, we expect that addition of calcium silicate on rice-cropped soil could have a positive potential in mitigating the greenhouse gases emissions.

By definition, global warming is a gradual increase in the overall temperature of the Earth's atmosphere generally attributed to the greenhouse effect caused by increased levels of carbon dioxide, chlorofluorocarbons, and other pollutants. Under agriculture system, greenhouse gases (GHG) increments are much debated, thus investigations are conducted to clarify the GHG sources and sinks. GHG emissions such as methane (CH₄), carbon dioxide (CO₂), nitrous oxide (N₂O), chlorofluorocarbons (CFCs) and tropospheric ozone have increased substantially due to industrialization and changes in agriculture and land-use. As such CH₄, CO₂ and N₂O all have significant natural and anthropogenic sources (IPCC, 1990) and estimating these gases require a guideline. As a result, Global Warming Potential (GWP) system was developed.

Global Warming Potential (GWP) was developed to allow comparisons of the global warming impacts of different gases. Specifically, it is a measure of how much energy the emissions of one ton of a gas will absorb over a given period of time, relative to the emissions of one ton of carbon dioxide. The larger the GWP, the more that a given gas warms the earth compared to carbon dioxide over that time period. Carbon dioxide (CO₂), by definition has a GWP of 1 regardless of the time period used, which is the gas being used as the reference. Carbon dioxide remains in the climate system since before: carbon

dioxide emissions cause increment in atmospheric concentrations of carbon dioxide that will last thousands of years. Meanwhile, methane (CH_4) is estimated to have a GWP of 28-36 over 100 years. CH_4 emitted today lasts about a decade on average, which is much less than CO_2 ; but CH_4 absorbs more energy than CO_2 . The net effect of the shorter lifetime and higher energy absorption is reflected in the GWP. Thus, methane GWP accounts for indirect effects noted that methane is an ozone precursor and ozone itself a greenhouse gas. Nitrous oxide (N_2O) has a GWP 265-298 times as much as that of CO_2 for a 100-year timescale. N_2O emitted today remains in the atmosphere for more than 100 years, on average (<https://www3.epa.gov/climatechange/ghgemissions/gwps.html>).

Methane (CH_4) is one of the most important greenhouse gases (GHG), accounting for approximately 20% of the global greenhouse effect (Weubbles and Hayhoe, 2002). It is estimated that global CH_4 emissions from rice fields are 31-112 Tg per year, contributing 5-19% of the global CH_4 emissions (IPCC, 2007). Methane production results from the anaerobic decomposition of organic compounds where CO_2 acts as inorganic electron acceptor. Microorganisms which are capable of reducing the energetically more favorable electron acceptors such as NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-} and SiO_3^{2-} may outcompete those (methanogens) using the less favorable electron acceptor such as CO_2 (Lovely et al., 2004). Therefore, CH_4 production could be lowered by supplying alternative electron acceptors like NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-} and silicate, which may result in a combination of inhibition effects and competitive effects with different microorganism for the common electron donors (Achnich et al., 1995). Direct agricultural sources of N_2O emissions include inorganic and organic forms of N added to soils as fertilizers, manures and composts. Some of inorganic N added to soils as fertilizers undergoes microbial nitrification and denitrification processes in soils and aquatic ecosystems, releasing N_2O to the atmosphere. Both processes produce N_2O in the presence of low concentration of O_2 at the transition between aerobic and anaerobic conditions in soils. During nitrification, N_2O is produced under aerobic conditions but the formation rates increase as O_2 concentration decreases. The relative proportion of N_2O in gaseous denitrification products increases as the O_2 concentration increases in an anaerobic environment. Major factors regulating nitrification and denitrification are the presence of reactive N, the availability of reductant (mostly labile organic carbon compounds), and oxygen concentration. These three factors are in

turn governed by many other factors such as water content, pH, porosity, and the presence of inhibitory compounds (Bouwman, 1996; Stehfest and Bouwman, 2006).

Soil oxidants and reductants play important roles in controlling CH₄ production and emission in wetland rice cultivation (Watanabe and Kimura, 1999). It is recognized that Fe oxides functions as a major oxidizing material and controls the production of CH₄ (Watanabe and Kimura, 1999) under submerged conditions. Silicate fertilizer, the byproduct of steel industry, contain high amount of active Fe and free Fe oxides and may be used as an oxidizing agent in wetland rice farming. In addition, this byproduct of steel industry provides adequate silicate ions that are necessary for higher rice productivity (Ma et al., 1989) and for inducing resistance to biotic and abiotic stresses (Takahashi et al., 1990). Ali et al. (2008) reported that silicate fertilizers, being potential sources of ferric Fe oxides, significantly reduced total CH₄ emission and increased rice productivity in pot and field experiments. According to Ali et al., (2009) total seasonal CH₄ flux was decreased at 20% in tillage and 36% in no-tillage plot, while grain yields were increased at 18% and 13%, respectively with application of 4 Mg ha⁻¹ silicate fertilization.

Water level may vary in the rice field area. Shallow water level is expected to decrease CH₄ emissions; however, there is a risk of increasing N₂O emissions while deep water level is expected to increase CH₄ emissions and reducing N₂O emissions. Soil amendments such as calcium silicate with high content of electron acceptors along with differences of water level at certain extent may minimize CH₄ and N₂O emissions.

In the current context of Malaysia, inadequate information is available about the ability of calcium silicate under different water level on GWPs of CH₄ and N₂O gases. In addition, less information available on the impact of calcium silicate in mitigating greenhouse gases emissions on rice-cropped soil. Consequently, the objectives of this chapter were to 1) evaluate the efficacy of calcium silicate on GHG emissions under different water level of rice-cropped soil and 2) determine the ability of calcium silicate on nitrous oxide emissions of cultivated rice.

6.2 Materials and methods

6.2.1 Experiment 1 (Incubation study)

6.2.1.1 Material preparation and treatments

The soil used in this experiment was rice-cropped soil obtained from Tanashi field (35°44'18.51" N 139°25'24.81"E) (Figure 6.1). The soil then was air-dried and passed 2 mm sieve. Hundred gram of soil was put in the 500 mL of conical flask. The treatments used were 0, 1, 2, 3 t ha⁻¹ calcium silicate, 2 water level of (1:1, shallow) and (1:2, deep) ratio (soil: water) and the set-up were exposed under 2 condition; i) with oxygen and, ii) without oxygen, with three replications. The soil was incubated in the incubator (Figure 6.2) at 25°C and 75% relative humidity throughout incubation period. The total unit are 48 (4 rate calcium silicate x 2 water level x 2 oxygen conditions x 3 replications).

For the experimental set-up with oxygen, the oxygen and nitrogen gases were supplied continuously for 35 days using gas blender (Kofloc, model Gasblender GB-3C) (Figure 6.3). Those gases were flow at flow rate of 120 mL min⁻¹. The top of conical flask was covered using silicon stopper with 3 holes. Those holes were for inlet, outlet and for gas sampling (Figure 6.4a). For the inlet and outlet, the holes were filled with tubing (PISCO URETHANE TUBING 6x4 UB-0640-B 15- T226E) while for the hole for sampling was covered with another silicon stopper (Silicon W CAPS). For the inlet, the tubing was place in the water while for the outlet, the tubing was placed 5 cm from the water surface. The presence of bubbles were checked regularly (Figure 6.4b). The tubing for outlet was closed during gas sampling.

For the experimental set-up without oxygen, the top pf conical flask was covered using silicon stopper with 1 hole (Figure 6.5). The hole was covered with silicon (Silicon W CAPS). This hole was for gas sampling. For this experiment, the conical flask was closed for entire the incubation period of 35 days.

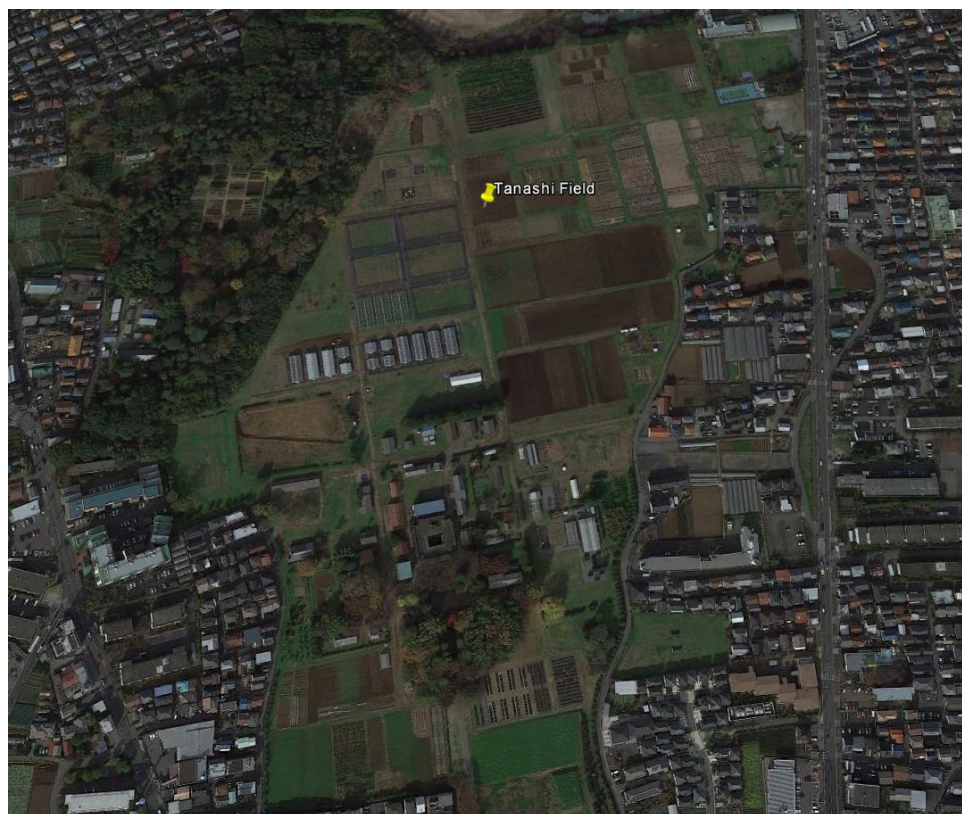
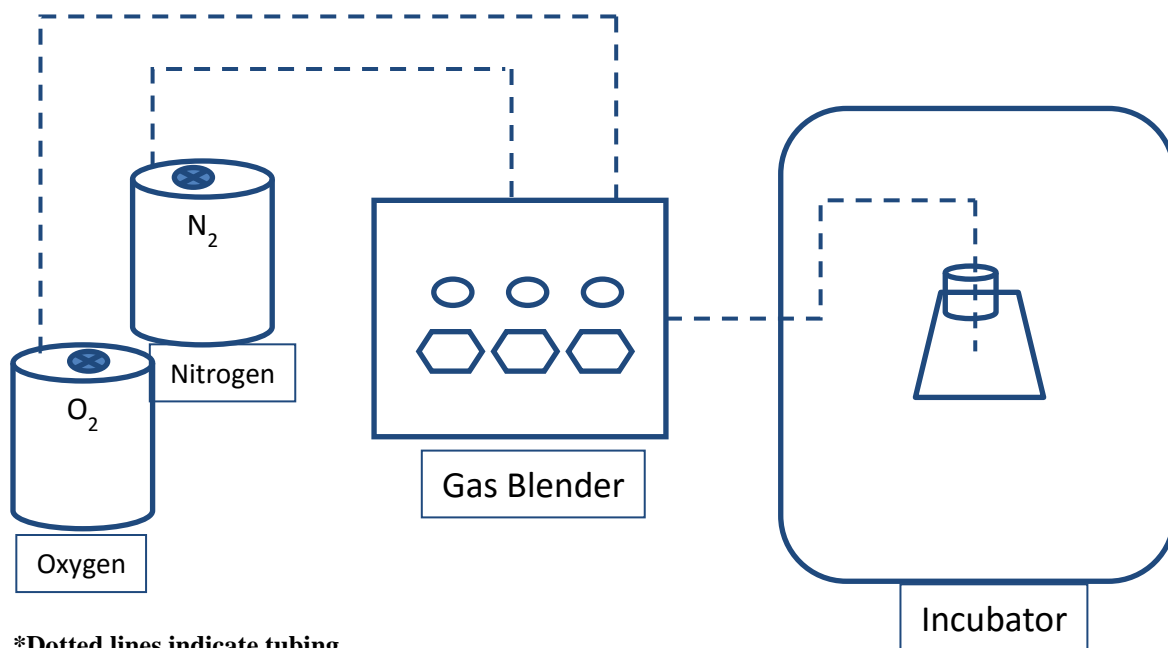


Figure 6.1 Satellite photo indicates Tanashi region, Nishitokyo, Japan, where the soil was obtained and used for this experiment (yellow pin). Source: Google earth. Location: Tanashi Field



Figure 6.2 The experimental set-up i) with oxygen supply (left) and, ii) without oxygen supply (right)



*Dotted lines indicate tubing

Figure 6.3 Schematic diagram on the experimental set-up with oxygen supply

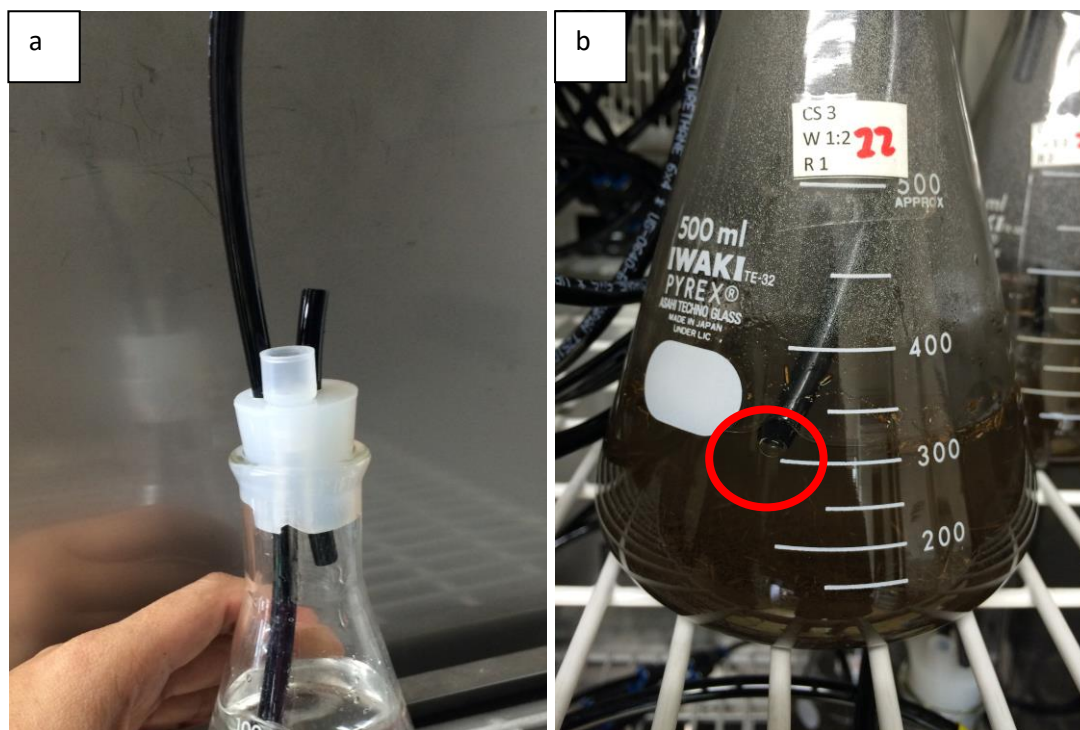


Figure 6.4 The experimental set-up with oxygen supply. Holes on the silicon stopper for inlet, outlet and gas sampling (a) and red circle indicate the presence of bubble (b)



Figure 6.5 The experimental set-up without oxygen. Hole on the silicon stopper for gas sampling

6.2.1.2 Gases sample collection and measurements

Air samples were withdrawn at 0 (0), 4 (0.17), 12 (0.5), 24 (1), 48 (2), 72 (3), 192 (8), 384 (16), 504 (21), 672 (28) and 840 (35) hours (days) after the beginning of the incubation process. The gas sampling were perform two times; i) 0 min sampling and, ii) 60 min later. The gas was sampled 30 mL using gastight syringe and transferred in the sampling bottles (15 mL) (SVF-15).

The gas samples were analyzed for methane, carbon dioxide and nitrous oxide. Methane and carbon dioxide were analyzed using gas chromatography system which was equipped with flame ionization detector (GC-FID) and thermal conductivity detector (GC-TCD) while nitrous oxide was measured by using gas chromatography with an electron capture detector (GC-ECD).

Soil CH₄, CO₂ and N₂O production in the container headspace was calculated according to equations used by Holland et al. (1999). Gas concentrations (ppm) obtained with the chromatography system was converted to mass units with the ideal gas equation:

$$C_m = (C_v * M * P) / (R * T)$$

Where C_m is the mass/volume concentration (e.g., mg CO₂-C m⁻³ incubation jar headspace), C_v is the volume/volume concentration (ppm of each GHG obtained with the chromatography system), M is the molecular weight of each GHG (e.g., 12 g CO₂-C mol⁻¹ or 28 g N₂O-N mol⁻¹), P is atmospheric pressure, R is the universal gas constant and T is the incubation temperature (298 K). C_m was multiplied by the headspace volume of the incubation containers (5 x 10⁻⁴ m³) to obtain the mass of CH₄-C, CO₂-C or N₂O-N accumulated during the incubation. Thus, the mass of GHG produced (e.g., mg CH₄-C kg⁻¹ soil h⁻¹) is calculated as follows:

$$F = ((C_1 - C_0) / (m * t)) * 1000$$

Where F is the mass of gas produced per unit time, C₁ and C₀ are the mass of C or N produced at the end and the beginning of two consecutive samplings, respectively, m is the mass of air-dried soil in each container (0.1 kg) and t is the incubation period (1h).

6.2.2 Experiment 2 (Glasshouse study)

6.2.2.1 Planting materials, treatments and experimental design

Twenty kilogram (20 kg) of soil was filled in the pot. The treatments used for this experiment were; (T1) control (without calcium silicate), (T2) 1 t ha⁻¹ calcium silicate, (T3) 2 t ha⁻¹ calcium silicate, (T4) 3 t ha⁻¹ calcium silicate and. (T5) bare soil with three replication arranged in randomized completely block design (RCBD) (Figure 6.6). Treatments were incorporated with soil at approximately 15 cm depth before water was added. After 24 hours, the rice seed was direct seeding into the soil. The variety of rice used in this experiment was Takanari. Only 1 seed per pot were cultivated. Water level was maintained regularly at 5 cm from the soil surface.

6.2.2.2 Gases sample collection and measurements

N₂O flux from the rice planted pot was measured by using closed chamber method (Rolston, 1986; Aliet al., 2009) every 7 days, starting from rice seeding until harvesting. The air gas samples from the transparent poly acrylic plastic chamber (110 cm height and 20 cm diameter) (Figure 6.7) were collected by 20 mL gastight syringes at 10 a.m (t₀) and at 11 a.m (t₆₀) after chamber placement. Nitrous oxide was measured using gas chromatography with an electron capture detector (GC-ECD). A closed chamber equation (Rolston, 1986) was use to estimate N₂O fluxes from each treatment.

$$F = \rho * V / A * \Delta c / \Delta t * 273 / T,$$

Where, F is the N₂O flux (mg N₂O m² h⁻¹), ρ is the gas density (0.714 mg cm⁻³), V is the volume of chamber (m³), A is the surface area of chamber (m²), $\Delta c / \Delta t$ is the rate of increase of nitrous oxide concentration in the chamber (mg m⁻³ h⁻¹), and T (absolute temperature) is the 273 + mean temperature in chamber (°C)

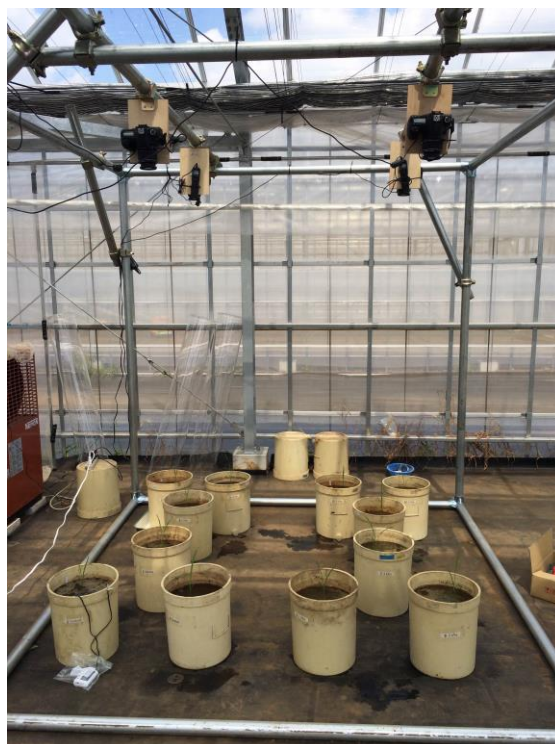


Figure 6.6 The experimental set-up of pot with 20 kg soil and Takanari rice variety

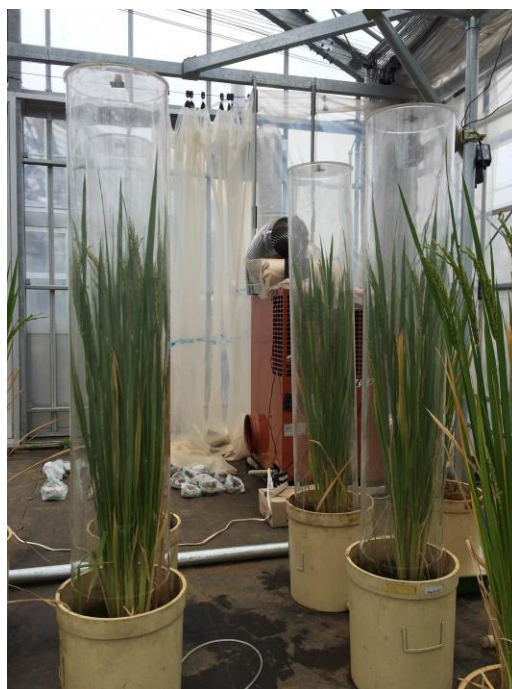


Figure 6.7 Gas sample collection using chamber at glasshouse

6.2.2.3 In-situ data measurements

Soil pH, oxidation-reduction potential (ORP) were measured using LAQUAact water quality meter, SPAD was measured using Chlorophyll Meter SPAD-502Plus, plant height was measured using measuring tape and tillers number were manually counted for each pot. The measurement for in-situ data was conducted for every 7 days interval from rice seeding until harvesting. Temperature of soil and water from bare soil treatment and soil with plant were measured for every 60 min interval throughout rice plant growth from seeding until harvesting using temperature sensors (TR-0106 x 2) (Thermo Recorder TR-71wf). Temperature and relative humidity were measured inside the glasshouse using Thermistor and Macromolecular Humidity Sensor, respectively (Illuminance UV Recorder TR-74Ui).

6.2.2.4 Relative importance of nitrification and denitrification in N₂O production from soil under different rate of calcium silicate

Soil samples from each experimental pot were collected at 30, 60, 90 and 120 days after seeding. The soil samples were sampled approximately at 0-15 cm depth from soil surface and were air-dried in the laboratory. The collected soil samples were sieved through 2 mm sieve. Ten gram (10 g) of soil samples were placed in 200 mL container and were moistened by distilled water at 1:1 (soil: water). The lids of the container were close and 30 mL headspace gas sample was taken for every jar (0 min sampling). Afterwards, acetylene (C₂H₂) treatment was applied: 0% and 5% (v v⁻¹) to differentiate the relative contribution of nitrification and denitrification processes in N₂O emissions (Klemetsson et al., 1988; Plaza-Bonilla et al., 2014).

Some drawbacks of the abovementioned method have been reported in the literature. Among them, Baggs (2008) enumerates (i) a possible underestimation of denitrification by preventing the supply of nitrifier-NO₃⁻, mainly in aquatic systems (Groffman et al., 2006), (ii) Acetylene could be used as a C-substrate for denitrification, and (iii) a limited diffusion of acetylene into fine textured soils.

The process were continued as, the container with the soil was incubated at 25°C for 24 hours. After that, another 30 mL of air was withdrawn to calculate the accumulation of N₂O in 24 hours period in each container. Air gas samples were stored and analyzed according to the same methodology as stated in Experiment 1 (sub-section 6.2.1.2). It was assumed that the N₂O measured in the treatment without

acetylene (i.e., 0% C_2H_2) corresponded to the N_2O produced by the nitrification and denitrification process and the N_2O measured in the treatment with a C_2H_2 concentration of 5% corresponded to the N_2O produced due to a complete denitrification (Yoshinari et al., 1977). The production of N_2O by nitrification process was calculated from difference between the N_2O measured in 0% and the 5% C_2H_2 treatments, while the production of N_2O by denitrification process corresponded to the amount of N_2O measured in 5% C_2H_2 treatment. The gas samples were analyzed with gas chromatography system equipped with an ECD detector (GC-ECD).

6.2.3 Statistical analysis

Statistical analysis for means comparison was performed using Tukey's test in SAS version 9.2 (SAS, Institute, Inc., Cary, NC).

6.3.1 Results

6.3.1 Experiment 1 (Incubation study)

Based on the incubation study, it is possible to postulate the effect of oxygen (O), water level (W), calcium silicate treatments (S), time (T) and their interactions on methane, carbon dioxide and nitrous oxide emissions. Their respective effects are shown in Table 6.1.

Table 6.1

Table of ANOVA on methane, carbon dioxide and nitrous oxide emissions

Source of variance	Methane (CH ₄)	Carbon dioxide (CO ₂)	Nitrous oxide (N ₂ O)
Oxygen (O)	4167.4 ***	3.487e+10***	20229.7 ***
Water level (W)	511.1 **	1.33e+9***	8460.3 ***
Calcium silicate (S)	30.5 ns	3.62e+8***	1100.2 ***
Time (T)	889.8 ***	1.91e+10***	5809.9 ***
S*W	226.3**	1.38e+8 *	507.8 *
S*O	33.2 ns	2.87e+8 ***	1106.8 ***
S*T	11.1 ns	3.3e+7 ns	309.7 ***
O*W	511.7 **	3.98e+7 ns	8115.8 ***
O*T	902 ***	6.75e+9 ***	5518.3 ***
W*T	141.2 **	2.02e+8 ***	2312.6 ***

*** $p < 0.0001$

** $p < 0.01$

* $p < 0.05$

ns – not significant

6.3.1.1 Oxygen influence

From Table 6.1, it is clearly shown that oxygen significantly influence the emission of GHG (methane, carbon dioxide and nitrous oxide) from the research soil. Furthermore, methane and carbon dioxide emissions decrease significantly under exposure of oxygen compared to during the absence of oxygen, while nitrous oxide emission was decreased significantly under condition without oxygen supply. The condition of oxygen supply was to replace the condition of rice root where the oxygen was available.

6.3.1.2 Water level influence

Two water level were used in this experiment, which are 1:1 (shallow) and 1:2 (deep) representing soil:water ratio. Based on the observation, it was shown that water level also influence methane, carbon dioxide and nitrous oxide emission significantly. From Table 6.1, methane emissions was reduced significantly under shallow water level while carbon dioxide and nitrous oxide under deep water level. Shallow and deep water levels were used in this study because these two water levels might occur in the paddy field.

6.3.1.3 Calcium silicate influence

It was also found that no significant effect was observed between calcium silicate on methane emission (Table 6.1). On the other hand, significant effect was observed on calcium silicate treatments for carbon dioxide and nitrous oxide emissions.

6.3.1.4 Time influence

Incubation time showed high influence on methane, carbon dioxide and nitrous oxide emissions (Table 6.1). methane and carbon dioxide were increased gradually noted with increment of incubation time after 12 hours until 840 hours. Meanwhile, a rapid increment of nitrous oxide emissions was observed for first 12 hours of incubation time and start to decreased from there on until 72 hours before the emissions becomes stable.

6.3.1.5 Interaction between calcium silicate and water level

Significant interaction between calcium silicate and water level was observed on methane, carbon dioxide and nitrous oxide emissions.

6.3.1.6 Interaction between calcium silicate and oxygen

Significant interaction between calcium silicate and oxygen was observed on carbon dioxide and nitrous oxide emissions and no significant interaction on methane emission.

6.3.1.7 Interaction between calcium silicate and time

Significant interaction was observed between calcium silicate and time on nitrous oxide emission while no significant interaction on methane and carbon dioxide emissions.

6.3.1.8 Interaction between oxygen and water

Significant interaction was observed between oxygen and water on methane and nitrous oxide while no significant interaction on carbon dioxide emission.

6.3.1.9 Interaction between oxygen and time

Significant effect was observed between oxygen and time on methane, carbon dioxide and nitrous oxide emissions.

6.3.1.10 Interaction between water and time

Significant effect was observed between water and time on methane, carbon dioxide and nitrous oxide emissions.

6.3.1.11 Methane, carbon dioxide and nitrous oxide emissions with time

Figure 6.8 show the methane (Figure 6.8 a and 6.8 b), carbon dioxide (Figure 6.8 c and 6.8 d) and nitrous oxide (Figure 6.8 e and 6.8 f) emissions throughout incubtion period under shallow and deep water levels with oxygen supply. On the other hand, Figure 6.9 shows the methane (Figure 6.9 a and 6.9 b), carbon dioxide (Figure 6.9 c and 6.9 d) and nitrous oxide (Figure 6.9 e and 6.9 f) emissions throughout incubtion period under shallow and deep water levels without oxygen supply. Consistent supply of oxygen through incubation period (time) showed low and stable emission of methane between 0.005 to 0.007 mg CH₄-C kg soil⁻¹ up to 840 hrs irrespective of water level (Figure 6.8a and 6.8b). Based on the result, it was shown that without oxygen supply, the methane emission ranged between 0.002 to 0.08 mg CH₄-C kg soil⁻¹ under shallow water level (Figure 6.9a) and 0.08 to 0.15 mg CH₄-C kg soil⁻¹ under deep water level (Figure 6.9 b). Without oxygen supply, the results showed that the methane emission begin to increase gradually at 192 hrs for both shallow and deep water levels. Under shallow water level, untreated soil and soil treated with 3 t ha⁻¹ calcium silicate were increased while under deep water level, all treatments were increased.

Continuous supply of oxygen through incubation period showed the carbon dioxide emission ranged from 1.76 to 49.36 mg CO₂-C kg soil⁻¹ under shallow water level (Figure 6.8c and 6.8d) and ranged from 2.07 to 38.39 mg CO₂-C kg soil⁻¹ under deep water level (Figure 6.9c and 6.9d). Under shallow water level, the carbon dioxide started to increase gradually at 12 hrs for all treatments (Figure 6.8c) while under deep water level similar scenario was observed except for soil treated with 2 t ha⁻¹ calcium silicate showed an erratic emission at 384 hrs (Figure 6.8d), while without oxygen supply, the carbon dioxide emission was ranged from 0.85 to 125.77 mg CO₂-C kg soil⁻¹ under shallow water level (Figure 6.9c) and from 0.95 to 111.78 mg CO₂-C kg soil⁻¹ under deep water level (Figure 6.9d). The carbon dioxide emission start to increase gradually after 12 hrs and increased rapidly after 72 hrs for both shallow and deep water levels.

Nitrous oxide emissions range from 0.002 to 0.52 for soil supplied with oxygen (Figure 6.8e and 6.8f) and from 0.002 to 0.03 N₂O-N kg soil⁻¹ for soil without oxygen (Figure 6.9e and 6.8f).

Soil samples supplied with oxygen showed spike of nitrous oxide at 12 hrs of incubation, with sharp decrease there on after until 48 hrs for all treatments under both shallow (Figure 6.8e) and deep (Figure 6.8f) water levels. The highest spike was for untreated soil with readings up to 0.5 mg N₂O-N kg soil⁻¹ under shallow water level and 0.15 mg N₂O-N kg soil⁻¹ under deep water level.

The results for without oxygen supplied showed that the nitrous oxide emission ranged from 0.0012 to 0.03 mg N₂O-N kg soil⁻¹ under shallow and from 0.0015 to 0.02 mg N₂O-N kg soil⁻¹ under deep water level. Under shallow water level showed spike of nitrous oxide at 24 and 840 hrs for all treatments. Under deep water level, nitrous oxide emission begin to increase gradually at 12 hrs and decrease there on after 48 hrs for all treatments while nitrous oxide emission was increased sharply at 672 hrs for soil treated with 2 and 3 t ha⁻¹ calcium silicate.

In absence of oxygen, the microbes consume oxygen from NO₃⁻ ions and thus it act as electron acceptor, and with that, rapid denitrification process leads to N₂ emission rather than N₂O. Thus, reducing the N₂O value in the incubation study flask. It was found that, presence of oxygen supplied was able to reduce nitrous oxide emissions under deep water (1:2) level compare to shallow (1:1) water level.

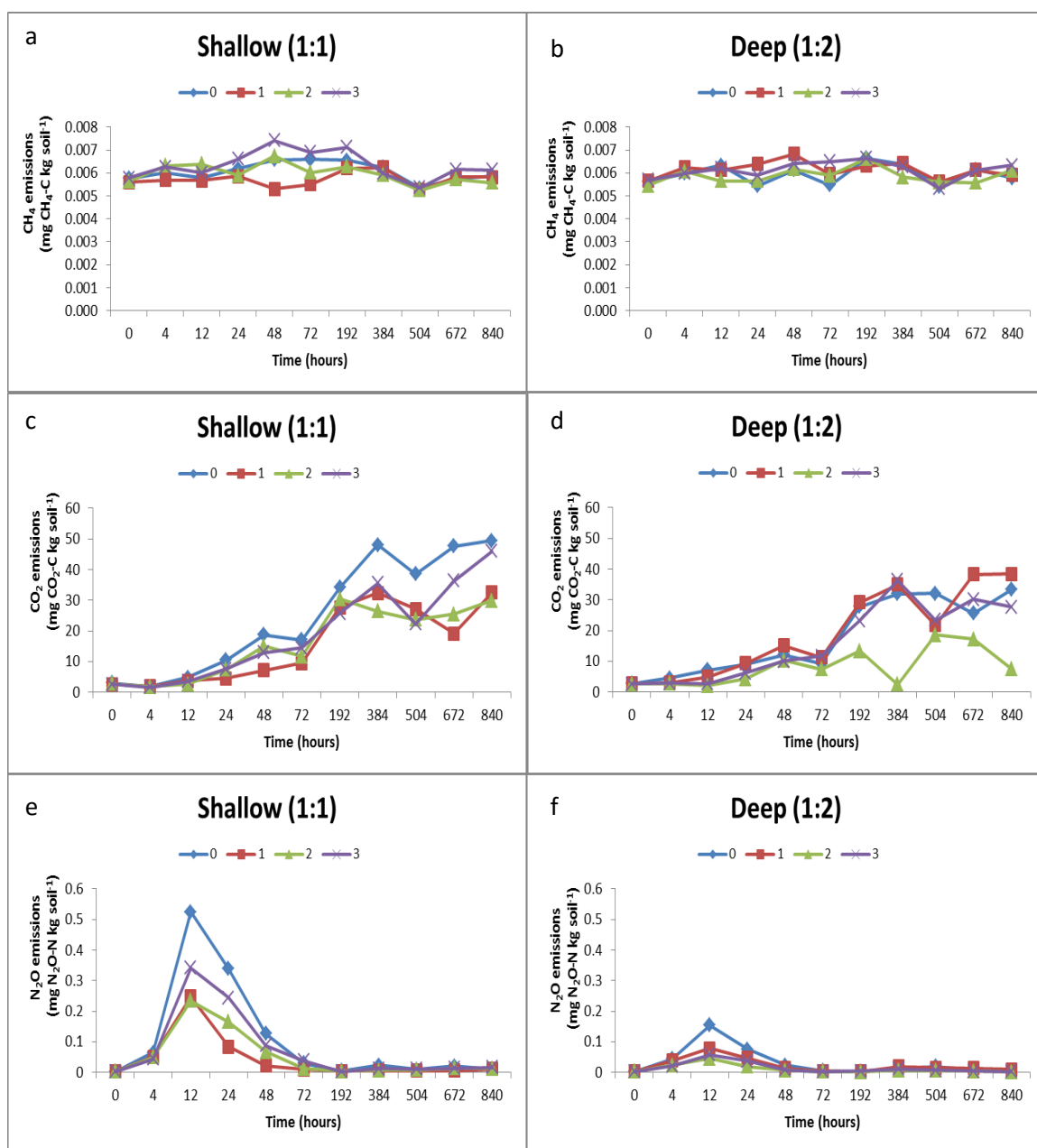


Figure 6.8 CH₄, CO₂ and N₂O emissions from soil as affected by calcium silicate (0, control; 1, 1 t ha⁻¹; 2, 2 t ha⁻¹ and 3, 3 t ha⁻¹) under shallow (W= 1:1) and deep (W= 1:2) water level with oxygen supply

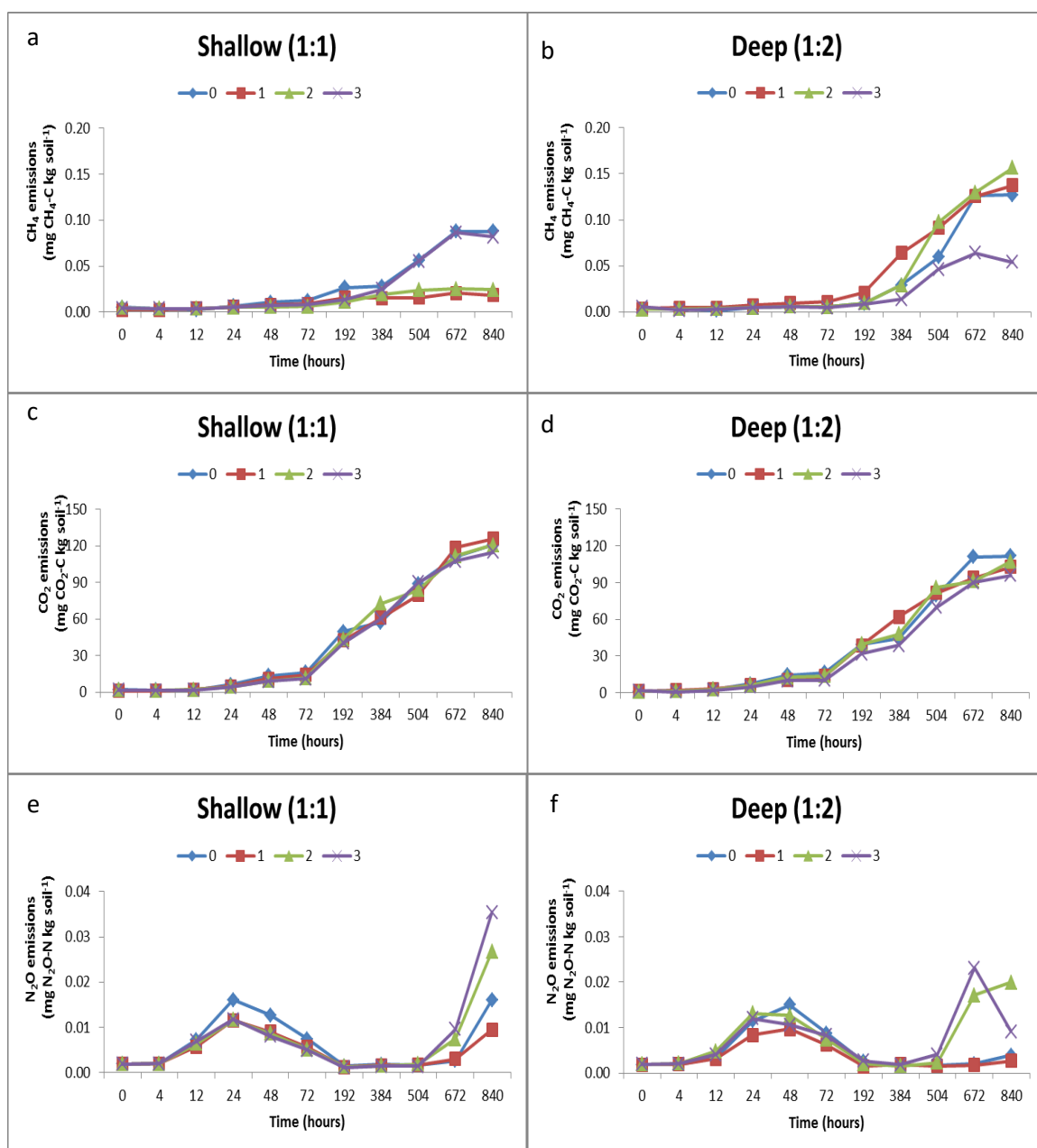


Figure 6.9 CH₄, CO₂ and N₂O emissions from soil as affected by calcium silicate (0, control; 1, 1 t ha⁻¹; 2, 2 t ha⁻¹ and 3, 3 t ha⁻¹) under shallow (W= 1:1) and deep (W= 1:2) water level without oxygen supply

6.3.1.12 Effect of calcium silicate on methane emissions under shallow and deep water levels with and/or without oxygen influence

Figure 6.10 shows the effect of calcium silicate on methane emission under shallow and deep water levels with oxygen supplied (Figure 6.10a) and without oxygen supplied (Figure 6.10b). Total methane emission was lower with oxygen supply (Figure 6.10a) ranged from 0.063 to 0.07 mg CH₄-C kg soil⁻¹ compared to without oxygen supply (Figure 6.10b) ranged from 0.12 to 0.50 mg CH₄-C kg soil⁻¹ irrespective both shallow and deep water levels (Figure 6.10).

For condition with oxygen supply, under shallow water level, no significant effect was observed between 0, 1 and 2 t ha⁻¹ calcium silicate on methane emission. On the other hand, soil treated with 3 t ha⁻¹ calcium silicate was significantly increased compared to 1 t ha⁻¹ calcium silicate value of 0.070 and 0.063 mg CH₄-C kg soil⁻¹, respectively. Under deep water level, no significant effect was observed among treatments on methane emissions value of 0.065, 0.068, 0.065 and 0.067 mg CH₄-C kg soil⁻¹ for 0, 1, 2 and 3 t ha⁻¹ calcium silicate, respectively.

For condition without oxygen supply, under shallow water level, no significant effect was observed between 0 and 3 t ha⁻¹ calcium silicate and between 1 and 2 t ha⁻¹ calcium silicate values of 0.326, 0.294, 0.116 and 0.132 mg CH₄-C kg soil⁻¹, respectively. Soil treated with 1 and 2 t ha⁻¹ calcium silicate were significantly reduced methane emission compared to untreated soil and soil treated with 3 t ha⁻¹ calcium silicate. Under deep water level, no significant effect was observed among the treatments on methane emission value of 0.376, 0.480, 0.132 and 0.294 mg CH₄-C kg soil⁻¹ for 0, 1, 2 and 3 t ha⁻¹ calcium silicate, respectively.

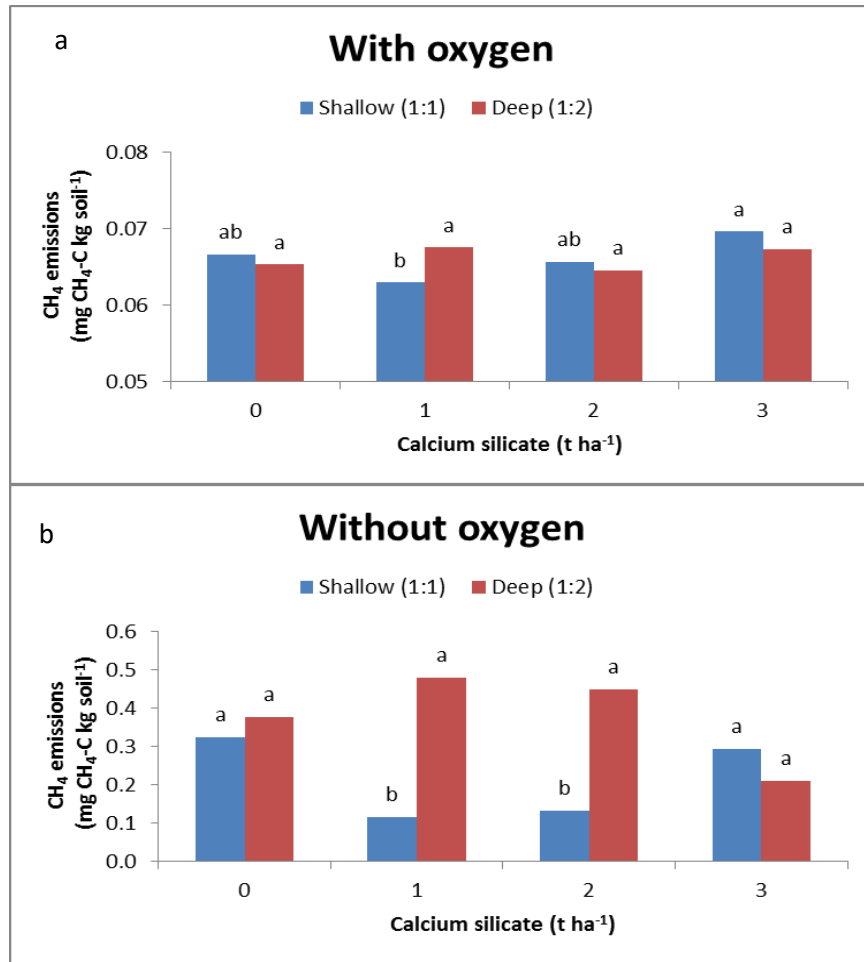


Figure 6.10 Effect of calcium silicate on methane emissions under different water level with oxygen (a) and without oxygen (b). Means marked with the same letter for each water level not significantly different at $p < 0.05$ (Tukey's Test)

6.3.1.13 Effect of calcium silicate on carbon dioxide emissions under shallow and deep water levels with and/or without oxygen influence

Figure 6.11 shows the effect on carbon dioxide emission under shallow and deep water levels with oxygen (Figure 6.11a) and without oxygen (Figure 6.11b). Total carbon dioxide emission with oxygen supplied was ranged between 88.33 to 271.39 mg CO₂-C kg soil⁻¹ and for condition without oxygen supplied was ranged between 356.08 to 468.70 mg CO₂-C kg soil⁻¹ irrespectively under both shallow and deep water levels.

For condition with oxygen supplied, under shallow water level, soil treated with 1 and 2 t ha⁻¹ calcium silicate were significantly reduced carbon dioxide emission compared to untreated soil. No significant effect was observed among soil treated with 1, 2 and 3 t ha⁻¹ calcium silicate values of 167.94, 177.08 and 208.42 mg CO₂-C kg soil⁻¹, respectively. Those treated soils were reduced the carbon dioxide emission from untreated soil by 38.56%, 35.22% and 23.76%, respectively. Under deep water level, no significant effect was observed between untreated and soil treated with 1 t ha⁻¹ calcium silicate and between 2 and 3 t ha⁻¹ calcium silicate. Soil treated with 2 and 3 t ha⁻¹ calcium silicate were significantly reduced carbon dioxide emission compared to untreated soil and soil treated with 1 t ha⁻¹ calcium silicate. Those soil treated with 2 and 3 t ha⁻¹ calcium silicate were significantly reduced carbon dioxide emission from untreated soil by 54.76% and 9.46%, respectively.

For condition without oxygen, under shallow water level, no significant effect was observed among treatments values of 468.70, 460.99, 463.16 and 442.15 mg CO₂-C kg soil⁻¹ for 0, 1, 2 and 3 t ha⁻¹ calcium silicate. Under deep water level, no significant effect was observed between untreated, soil treated with 1 and 2 t ha⁻¹ calcium silicate and between soil treated with 1, 2 and 3 t ha⁻¹ calcium silicate. Soil treated with 3 t ha⁻¹ calcium silicate was significantly reduced carbon dioxide emission by 17.13% from untreated soil.

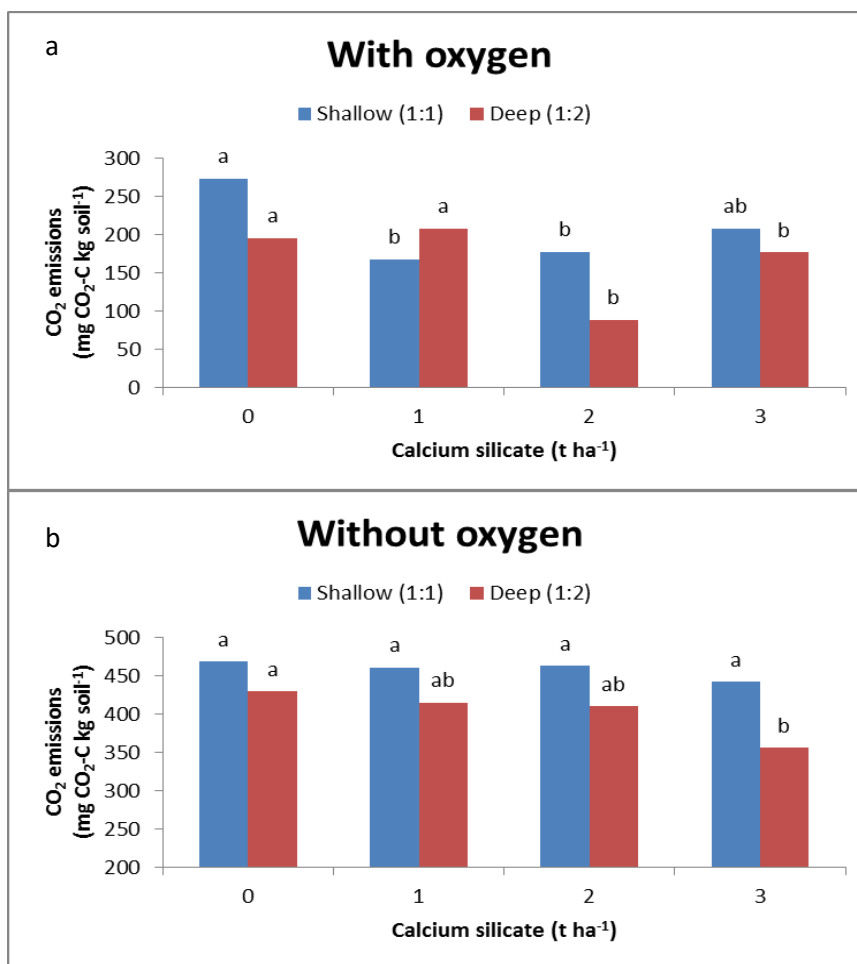


Figure 6.11 Effect of calcium silicate on carbon dioxide emissions under different water level with oxygen (a) and without oxygen (b). Means marked with the same letter for each water level not significantly different at $p < 0.05$ (Tukey's Test)

6.3.1.14 Effect of calcium silicate on nitrous oxide emission under shallow and deep water levels with and/or without oxygen influence

Figure 6.12 shows the effect of calcium silicate on nitrous oxide emission under shallow and deep water level with oxygen (Figure 6.12a) and without oxygen (Figure 6.12b). Total nitrous oxide emission with oxygen supplied ranged from 0.447 to 1.156 mg N₂O-N kg soil⁻¹ and for without oxygen supplied ranged from 0.117 to 0.352 mg N₂O-N kg soil⁻¹.

For condition with oxygen supplied, under shallow water level, soil treated with 1 and 2 t ha⁻¹ calcium silicate were significantly lowered nitrous oxide emission compare to untreated soil. No significant effect was observed between soil treated with 1, 2 and 3 t ha⁻¹ calcium silicate on nitrous oxide emission and those treatments were reduced nitrous oxide emissions compared to untreated soil by 61.33%, 50.42% and 29.71%, respectively. Under deep water level, no significant effect was observed between soil treated with 1 and 3 and between 2 and 3 t ha⁻¹ calcium silicate. Soil treated with 1, 2 and 3 t ha⁻¹ calcium silicate were significantly reduced nitrous oxide emission compared to untreated soil by 31.06%, 66.83% and 55.67%, respectively.

For the condition without oxygen, under shallow water level, no significant effect was observed among the treatments values of 0.0704, 0.0524, 0.0742 and 0.0843 mg N₂O-N kg soil⁻¹ for 0, 1, 2 and 3 t ha⁻¹ calcium silicate, respectively. Under deep water level, no significant effect was observed between 0, 2 and 3, between 0 and 1 and between 2 and 3 t ha⁻¹ calcium silicate. Soil treated with 2 and 3 t ha⁻¹ calcium silicate were significantly increased the nitrous oxide emission compared to soil treated 1 t ha⁻¹ calcium silicate by 57.17% and 47.10%, respectively.

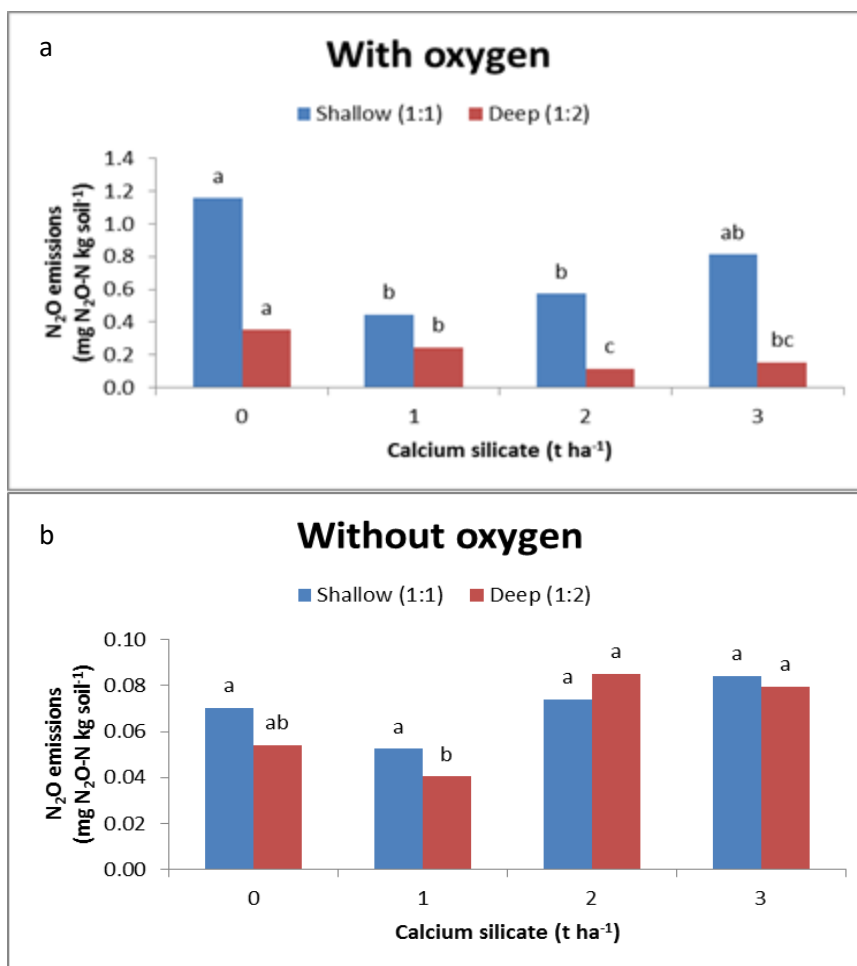


Figure 6.12 Effect of calcium silicate on nitrous oxide emissions under different water level with oxygen (a) and without oxygen (b). Means marked with the same letter for each water level not significantly different at $p < 0.05$ (Tukey's Test)

6.3.2 Experiment 2 (Glasshouse study)

6.3.2.1 Effect of calcium silicate on soil pH and ORP

Figure 6.13 show on soil pH throughout rice cultivation from seeding until harvesting period. The lowest and highest soil pH recorded were 6.53 and 8.54. The soil pH was gradually decreased from 14 DAS to 35 DAS for cultivated pot and it increased again from 35 DAS to 49 DAS. It was shown soil with rice plant have higher soil pH compare to bare soil from 56 DAS until harvesting except on 91 DAS. Drastic changes in pH can occur as a consequence of the microbially-mediated oxidation of nitrogen (Hinsinger et al., 2009). This is explained by: (i) the necessary release by plant roots of an H^+ ion when they absorb a NH_4^+ ion to counterbalance the corresponding excess of positive charges (Hinsinger et al., 2003); (ii) conversely, the release of OH^- ions when plant absorb NO_3^- ions to counterbalance the corresponding excess of negative charges, the excess OH^- being also partly neutralized by the 'biochemical pH-stat' (Raven 1986). Decreasing soil pH in bare soil was due to the applied fertilizer not being absorbed by the growing plant roots but accumulated and increased the EC in the soil solution (Okada and Fischer, 2001; Yanai et al., 1995)

Figure 6.14 show that oxidation-reduction potential (ORP) from seeding until harvesting period. The soil redox potential (Eh) for the bare soil was positive (+) from 1 DAS until 119 DAS. The soil redox potential for the cultivated soil was decreased gradually. The intense reductive condition was observed during flowering (84 DAS) until maturity phase and the soil redox potential close to and/or below zero (0). Decreased in soil redox potential might be due to the decomposition of soil organic matter. An increment in soil organic matter leads to a lowering of soil Eh: in soils rich in easily decomposable organic matter, oxidation processes consume large amounts of oxygen, which leads to the formation of organic compounds with reducing properties (Lovley et al., 1998).

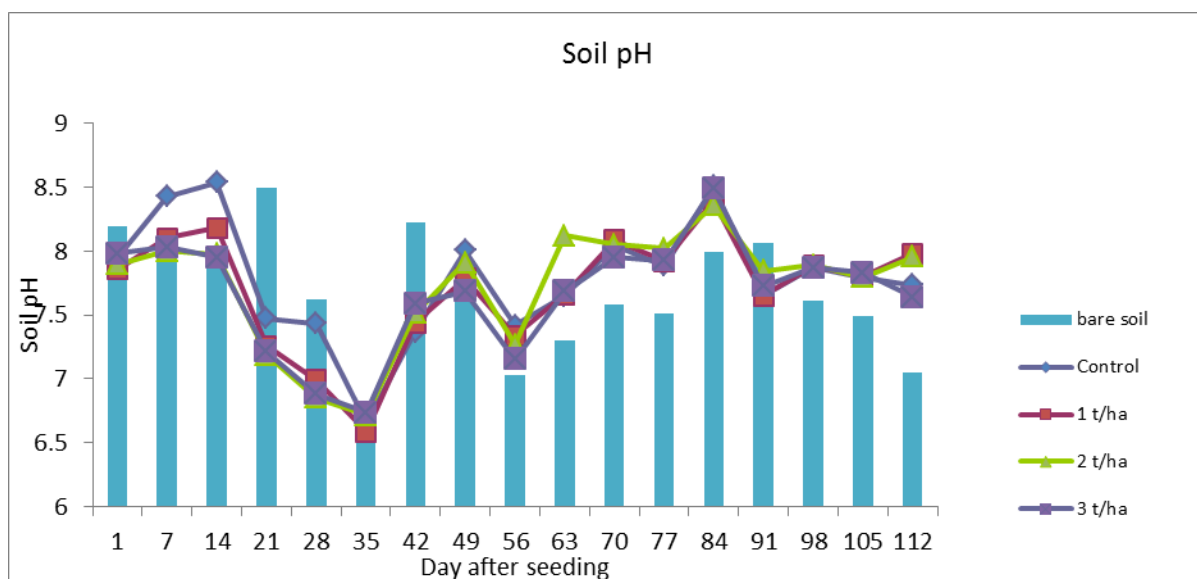


Figure 6.13: Effect of treatments on soil pH throughout rice planting

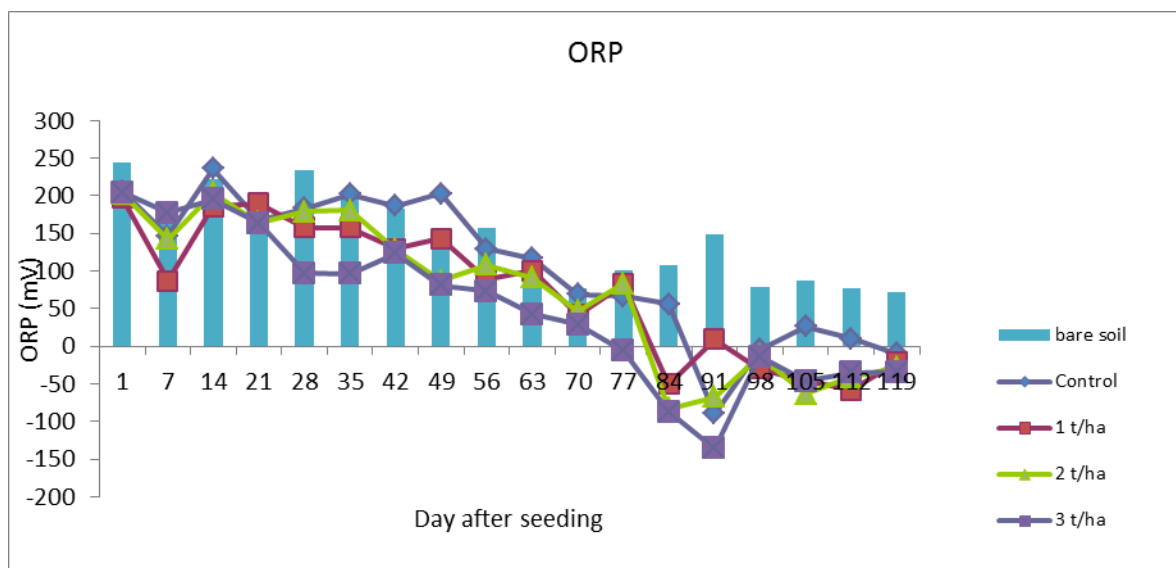


Figure 6.14 Effect of treatments on ORP value throughout rice planting

6.3.2.2 Effect of calcium silicate on selected plant-growth parameters (SPAD, tillers number and plant height)

Figure 6.15 shows the effect of calcium silicate on the SPAD reading from 14 DAS until harvesting period. The SPAD reading was increased gradually from 14 DAS to 42 DAS. The SPAD reading was ranged between 36.4 to 44.56, between 39.2 to 44.96, between 40.63 to 45.6 and between 39.1 to 45.6 for 0 (control), 1, 2 and 3 t ha⁻¹ of calcium silicate fter 42 DAS until 98 DAS, respectively. After 98 DAS, the SPAD reading was gradually decreased for all treatments. 119 DAS recorded the lowest SPAD reading value of 28.06, 27.80, 28.56 and 27.46 for 0 (control), 1, 2 and 3 t ha⁻¹ calcium silicate, respectively. This is because the plant were almost to reach maturity phase and the rice leaves was decaying

Figure 6.16 shows the effect of calcium silicate on the tillers number from 7 DAS until harvesting period. The tillers number were remained 1 from 7 DAS until 21 DAS for all treatments. Thereafter, the tillers number were increased gradually until 56 DAS. Maximum tillers number produced was at 56 DAS value of 26, 24.33, 24 and 25 for 0 (control), 1, 2 and 3 t ha⁻¹ calcium silicate, respectively. At 119 DAS, tillers number slightly decreased compare to maximum tillering (56 DAS) for all treatments (Figure 6.16) because unproductive tillers were degraded and only productive tillers were remained.

Figure 6.17 shows the effect of calcium silicate on the plant height throughout the rice planting. The plant height gradually increased from seeding until 98 DAS and thereafter the plant height was remained similar until harvesting. The maximum plant height was recorded at 98 DAS value of 103.66, 103.80, 104.5 and 101.50 cm for 0 (control), 1, 2 and 3 t ha⁻¹ calcium silicate, respectively.

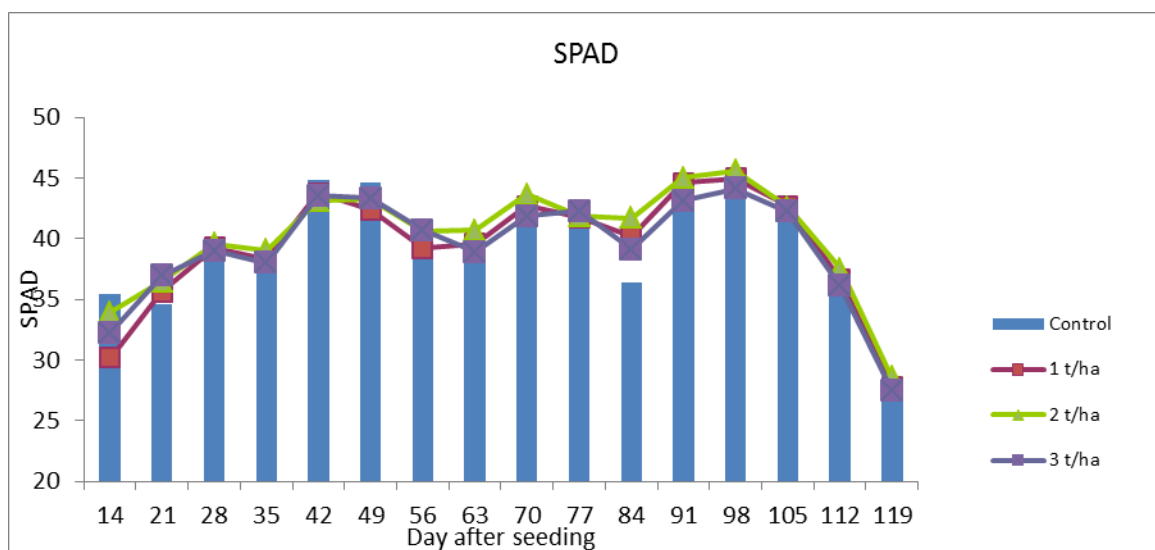


Figure 6.15 Effect of treatments on SPAD throughout rice planting

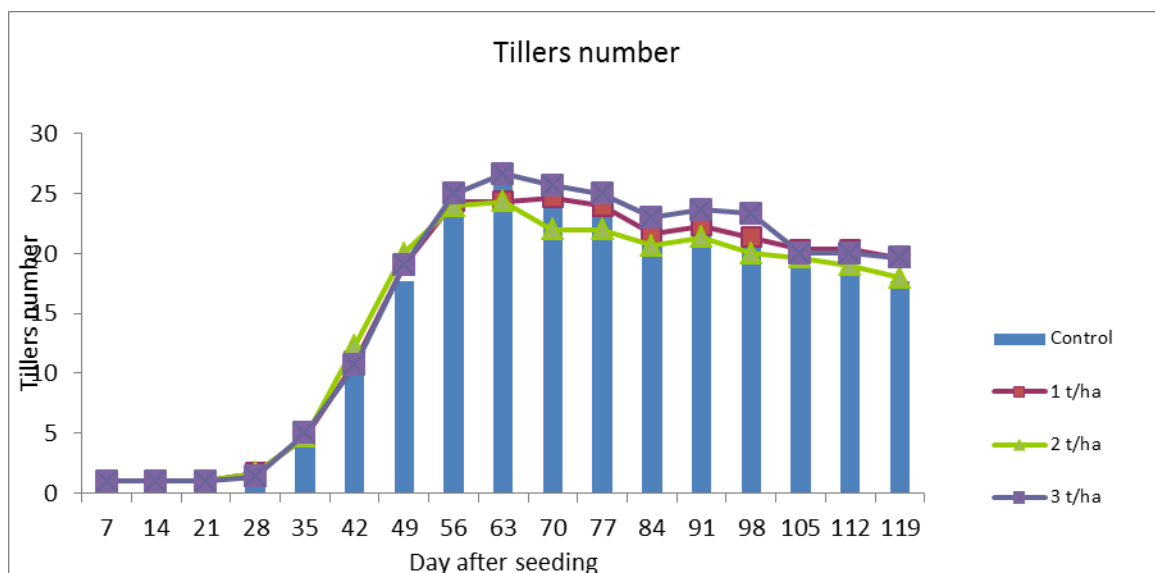


Figure 6.16 Effect of treatments on tillers numbers throughout rice planting

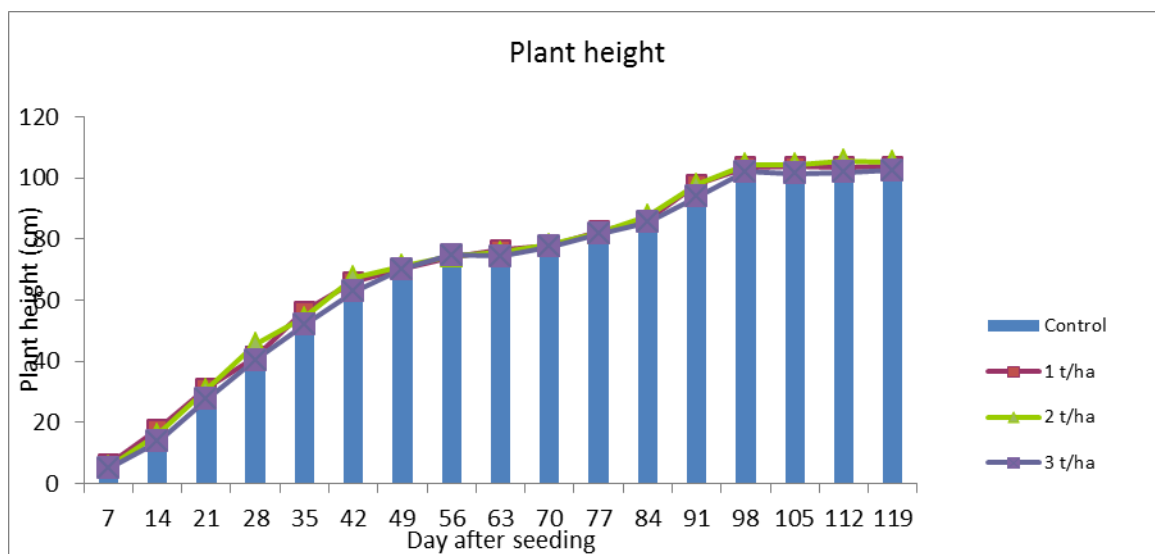


Figure 6.17 Effect of treatments on plant height throughout rice planting

6.3.2.3 Temperature and relative humidity

Figure 6.18 and 6.19 show the temperature of water and soil, respectively for both in unplanted soil (bare soil) and planted soil. Highest water temperature of bare soil was 42°C while lowest was 13.8°C, respectively. Meanwhile, soil temperature of bare soil was 42.5°C (highest) and 12.8°C (lowest). The average temperature for water and soil of bare soil were 26°C and 25.5°C, respectively. Highest temperature in water and soil of cultivated soil were 39.2°C and 40.9°C while lowest temperature were 12.8°C and 11.5°C, respectively. Average temperature for water and soil of cultivated soil were 25.2°C and 24.6°C

Figure 6.20 and 6.21 show the temperature and relative humidity in the glasshouse. The highest temperature recorded was 46.7°C while lowest temperature was 10.6°C with the average temperature 23.82°C. Highest and lowest relative humidity recorded were 100% and 19.8%, respectively. Average relative humidity was 81.55%.

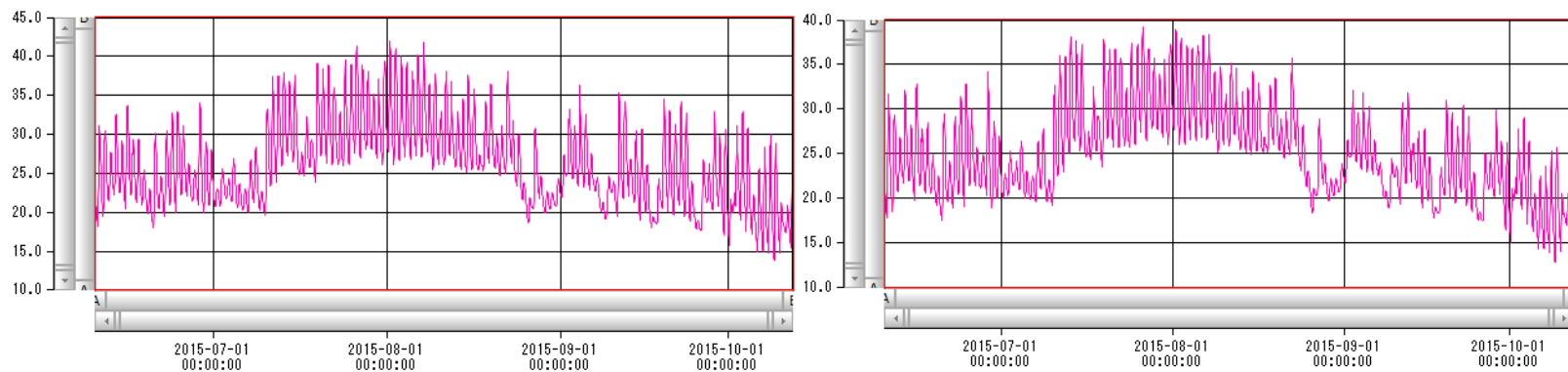


Figure 6.18 Water temperature of bare soil (left) and cultivated soil (right)

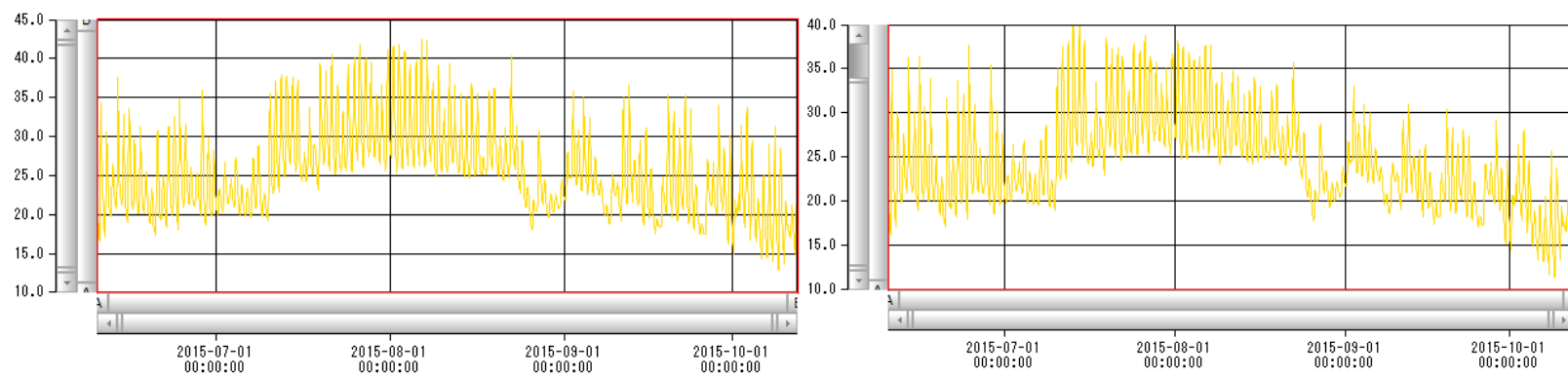


Figure 6.19 Soil temperature of bare soil (left) and cultivated soil (right)

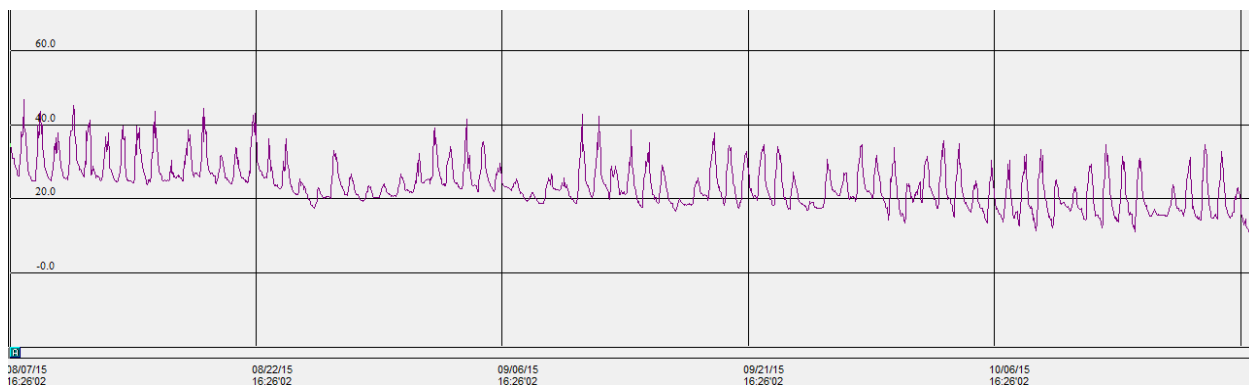


Figure 6.20 Temperature (°C) inside the glasshouse

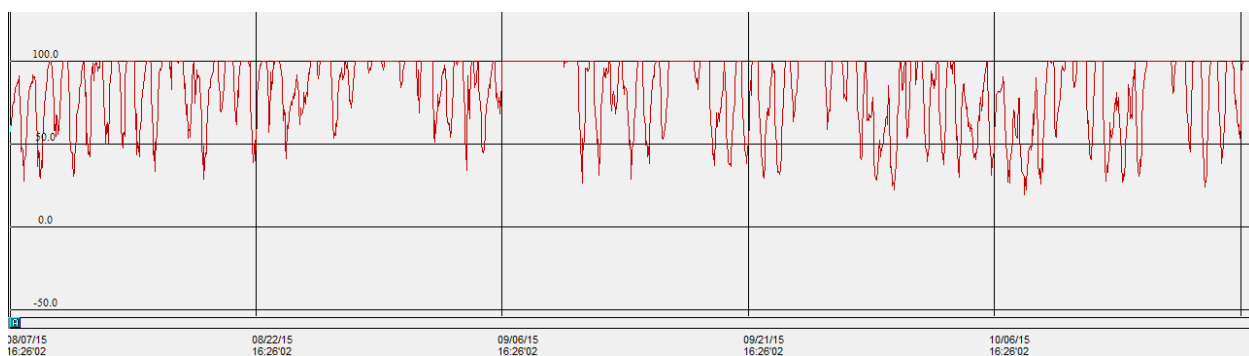


Figure 6.21 Relative humidity (%) inside the glasshouse

6.3.2.4 Cumulative nitrous oxide emission of anaerobic rice throughout rice planting

Figure 6.22 show the N₂O emission from treatments of anaerobic rice. The lowest N₂O emission was from the bare soil followed by the control treatment and soil treated with 2 t ha⁻¹ of calcium silicate. No significant effect was observed among these three treatments. However, N₂O emissions from control treatment were higher compare to bare soil. It was shown that, rice plant plays the main role in contributing on N₂O emission. Addition of calcium silicate stimulates N₂O emission or it can be said calcium silicate was N₂O stimulator. Soil treated with 1 and 3 t ha⁻¹ calcium silicate was significantly higher than control and bare soil. Soil treated with 2 t ha⁻¹ of calcium silicate was significantly depressed the N₂O emission by 67.64% compare to soil treated with 3 t ha⁻¹ of calcium silicate.

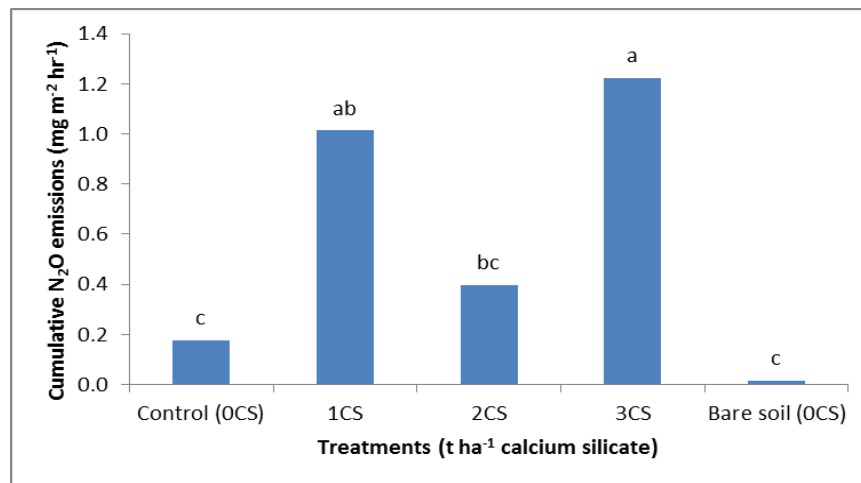


Figure 6.22 Cumulative nitrous oxide emissions of anaerobic rice

6.3.2.5 Effect of treatments on N₂O emission through nitrification and denitrification

Figure 6.23 show the effect of treatments on N₂O emission from nitrification and denitrification processes. The production of N₂O due to denitrification was greater compare to nitrification processes for all treatments. N₂O emission due to nitrification was significantly higher for soil treated with 3 t ha⁻¹ of calcium silicate compared to control, and soil treated with 1 t ha⁻¹. On the other hand, N₂O emission due denitrification, was significantly increased with soil received 3 t ha⁻¹ of calcium silicate compared to control and bare soil.

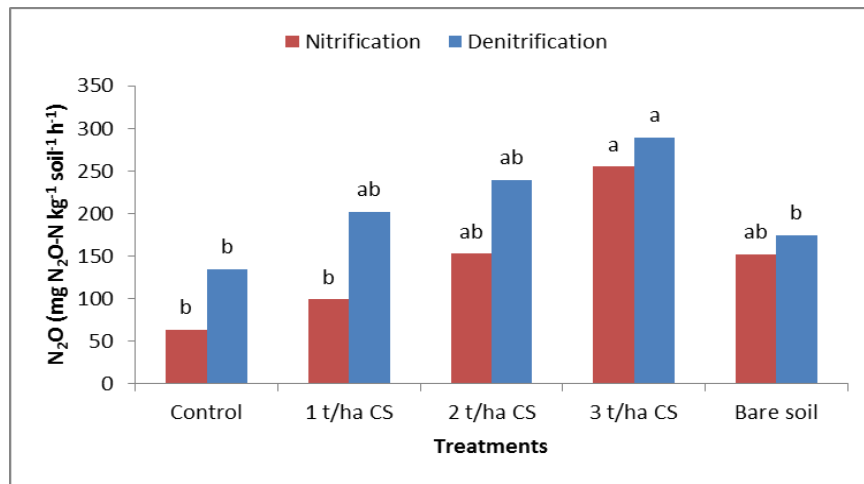


Figure 6.23 Effect of treatments on N₂O emission through nitrification and denitrification

6.4 Discussion

6.4.1 Methane emissions with and/or without oxygen and different water level

Methane emission was significantly low with presence of oxygen compared to absence of oxygen. Presence of oxygen was believed to replace the condition of root rhizosphere oxidative condition, with accelerated methane oxidation and reduced methane emission. Mechanism for gas emission from rice fields includes diffusion through the soil, ebullition and transport through the aerenchyma system of rice plants as stated by Holzapfel-Pschorn et al. (1985) and Wassmann and Aulakh (2000). Transport through the plants system is the major pathway for both CH₄ and N₂O emission as stated by Yu et al. (1997). Thus, CH₄ can be emitted from the soil to the atmosphere by diffusion and ebullition because of lower CH₄ solubility in water (1.48 mM in saturation at 20°C). CH₄ emissions from this study were thru ebullition and diffusion and this is consistent with no significant effect that was observed for CH₄ emissions under deep (1:2) water level from this study.

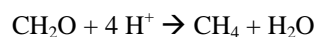
The result from this study showed that CH₄ emissions were significantly depressed with continuous oxygen supply compared to without oxygen supply. This situation is similar to the condition, in which the silicate (Si) is applied (becomes available for plant uptake), Si increases the rigidity and volume of aerenchyma (air-filled spaces in roots and shoots) that favors the transport of oxygen into the roots (Ma and Takahashi, 1990; Meena et al., 2013). Thus, increment in oxygen movement through aerenchyma from shoot to root (rhizosphere), leads to increment in methane (CH₄) oxidation. When more methane is oxidized, less methane is being emitted, thus reduction in methane emission (Hanson, 1980). Shallow water level significantly reducing CH₄ emission, because more CH₄ oxidation occurred and less CH₄ production in the smaller portion of the soil. The shallow water level aerated the soil surface layers, thus strictly reducing conditions could only be established at deep water level where the reducing intensity was strong enough to initiate significant CH₄ production. This finding is consistent with Yu et al. (2004) where non-flooded treatments were expected to significantly reduce CH₄ emission.

6.4.2 Plausible mechanism of calcium silicate efficacy to reduce CH₄ emission

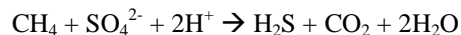
Calcium silicate was used in the study, instead of silicate slag fertilizer. The difference is that, the former is believed to have trace amount of ferric ion (Fe³⁺) and sulfate ion (SO₄²⁻) that act as electron acceptor, compared to the latter that is known to have significant amount of both ions. Therefore, possibly if silicate slags fertilizer was used in this study, more CH₄ would be depressed.

The lower CH₄ emission from the soil treated with 1 and 2 t ha⁻¹ calcium silicates under shallow water level was due to increased aeration and stabilization of soil C, improved soil redox potential status, higher content of active iron oxides, increased sulfate and nitrate ionic compounds, which acted as electron acceptors and eventually suppressed CH₄ production.

This implies that the soil amendments used containing electron acceptors such as ferric iron (Fe³⁺) and sulfate (SO₄²⁻) that potentially affects CH₄ production through the following reaction:



From the above reaction, it is obvious that 4 mol of Fe³⁺ iron inhibit generation of 1 mol of CH₄. Similarly, sulfate (SO₄²⁻) act as electron acceptor and reduce methane production through the oxidation of CH₄ to CO₂ as follow:



This mechanism was supported by Patrick et al. (1973), Inubushi et al. (1984) and Lovely and Philips (1987).

From this study, it show that increasing amount of calcium silicate increase both CH₄ (Figure 6.10) and CO₂ emission (Figure 6.11). However, it contradicts with finding by Ali et al. (2009); CH₄ production decrease significantly, whereas CO₂ production increase significantly with additional usage of soil amendment.

6.4.3 Nitrous oxide emissions

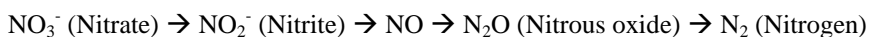
1. Rice soils are acknowledged as N_2O producer; if the rice field is not continuously flooded. This is because ammonium (NH_4^+) and nitrate (NO_3^-) are available from fertilization by which temporary oxidizing conditions enable nitrification (conversion NH_4^+ to NO_3^-) to take place as stated by Byrnes et al. (1993).

Nitrous oxide can be produced from nitrification under aerobic conditions (observed with high Eh) and denitrification (reduction of NO_3^- to N_2O and N_2) under moderately reducing conditions (lower Eh) where the reduction intensity is not strong enough to completely reduce nitrate to nitrogen gas (N_2). Factors such as coupled nitrification/denitrification at the two aerobic/anaerobic interfaces water/soil and rice plant rhizosphere/bulk soil, are an important mechanism of N loss and N_2O production in rice fields (Arth et al., 1998)

2. High N_2O released due to denitrification of NO_3^- .

Under aerobic condition, nitrifiers (nitrosomonas and nitrobacter) will convert NO_3^- to NO_2^- , then quickly to N_2O . This process is only applicable at pH 6.0 and above, but under acidic condition, at pH < 5, nitrifiers activity becomes negligible. Thus, chemoheterotrophic bacteria play the role of denitrification under acidic and anaerobic condition (flooded rice under acidic soil of pH<5). Chemoheterotrophic bacteria which is aerobes needs oxygen but oxygen is very minimal. Thus, it converts NO_3^- to N_2O , and consumes the oxygen from the conversion process. Thus, anaerobic condition of acid soils favors denitrification process by chemoheterotrophic bacteria.

The conversion of NO_3^- to NO_2^- and fastly to N_2 as shown below:



In flooded rice (anaerobic condition), mainly N_2O (gas) is released, where pH is about 4.7 (pH<5) meanwhile, N_2 (gas) only will be produced when the pH is above 6.0.

Two conditions are require for chemoheterotrophic bacteria to do the conversion which are i) presence of oxygen, by which oxygen is an electron acceptor and, ii) source of C for the microbes.

3. under anaerobic condition (flooded rice), oxygen demand exceeds supply, also known as very minimal oxygen, and thus the microbe (known as chemoheterophilic bacteria) uses NO_3^- as electron acceptor instead of oxygen. When NO_3^- becomes electron acceptor (it becomes oxidizing agent) by accepting electron, it converts NO_3^- to NO_2^- , then quickly to N_2O (gas), because NO_2^- is unstable and toxic to plant. Increment in NO_3^- as electron acceptor is noted with positive value (+ mV) and increase in ORP that justify the function of NO_3^- as electron acceptor substituting the need of oxygen like in aerobic condition.

This is known as anaerobic microenvironment condition. And, plant root exudates become carbon (C) source for the chemoheterotrophic reaction to occur, and thus immobilize NO_3^- . The uptake and release explained as root diffusion (i.e rhizosphere respiration reacts with OH^- and CO_2 to form HCO_3^-).

Furthermore, the reduction of NO_3^- and oxidation to N_2O show redox reaction. Plus, plant root growth may also serve as sink for NO_3^- . Thus, to some extent inhibit NO_3^- denitrification through roots (rhizosphere). If plant absorbs NH_4^+ greater than NO_3^- , H^+ excreted this can lower pH in the rhizosphere. The excreted H^+ can react with NO_3^- accumulated at root rhizosphere and forms HNO_3 . HNO_3 is also an oxidizing agent. Thus, higher presence of oxidizing agent leads to increment in ORP value. If plant adsorbs NO_3^- greater than NH_4^+ , OH^- excreted and increase pH of rhizosphere. It will cause excess OH^- can neutralize excess H^+ under acidic condition.

4. Nitrification process is controlled by the O_2 partial pressure, $\text{NH}_3/\text{NH}_4^+$ concentration and pH (Tiedje 1988). These factors are affected by presence of plant roots in the soil. The O_2 partial pressure can be changed by respiration of roots and root-associated microorganism. Root consumption of water and penetration creates channels (macro/biospheres) for gaseous transfer. Besides that, plants also release readily available organic compounds in the soil solution through rhizodeposition, which become major sources of microbial nutrients in the rhizosphere.

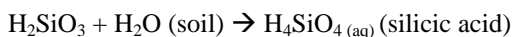
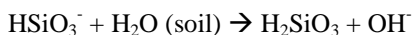
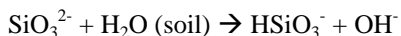
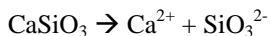
6.4.4 Plausible mechanism on the N₂O production from the soil cultivated with paddy

Nitrate (NO₃⁻) anion is a product from nitrification process, and calcium (Ca²⁺) cation are dissociated from application of calcium silicate (CaSiO₃) to the soil. Both anion and cation are taken up (adsorbed) by plant. In relation to that condition, rice roots adsorb more Ca²⁺ compared to NO₃⁻. Thus, competition between Ca²⁺ and NO₃⁻ can occur in soil treated with 1 t ha⁻¹ calcium silicate. When this happen, rice plant will first uptake macronutrients that is Ca²⁺ in higher quantity compared to NO₃⁻. Thus, more NO₃⁻ will remain in the soil system. Since NO₃⁻ is not stable, it will undergo denitrification process, thus give rise to N₂O.

At 2 t ha⁻¹ of calcium silicate, the soil system was found to be at equilibrium. It means that most probably NO₃⁻ and Ca²⁺ in the soil are equally available for plant uptake, thus reduce the competition between Ca²⁺ and NO₃⁻ for uptake. This is plausible that less NO₃⁻ presence for N₂O production due to denitrification. And, at 3 t ha⁻¹ of calcium silicate, Ca²⁺ increase and competition once again can occur between Ca²⁺ and NO₃⁻. As Ca²⁺ is taken up by plant, NO₃⁻ remains in excess, thus undergo denitrification process (Figure 6.23), and hence release more N₂O.

6.4.5 Silicate as electron acceptor

Calcium silicate was applied into soil as soil amendment. The chemical formula for calcium silicate is CaSiO_3 . Upon dissolution in soil, calcium silicate release calcium (Ca^{2+}) and silicate (SiO_3^{2-}) ions in the soil solution. Silicate (SiO_3^{2-}) anion is an electron acceptor. It may function similarly to NO_3^- anion in soil system as an electron acceptor and oxygen donor. The calcium silicate dissolution process is shown in the below reaction:



Silicic acid is an organic acid.

Under the anaerobic condition (flooded rice), absence/minimal availability of NO_3^- , SiO_3^{2-} can act as additional electron acceptor substituting NO_3^- where necessary. This is plausible, that it give rise to denitrification process as noted in Figure 6.22. With increment of calcium silicate in soil (at 3 t ha^{-1}), rise in N_2O were clearly noted. In addition to that, Figure 6.23 also shows increase in denitrification process.

Besides that, high levels of silicic acid (H_4SiO_4) from calcium silicate dissolution can be used as a nutrient source for plants, and reduce disease attack (i.e rice blast) due stronger cell walls of plant (Abed-Ashtiani et al., 2012). Silicic acid is a water-soluble substance, thus their effect on soils system and plants are often prominent compared to application of GML and/or basaltic rocks application only. Consecutive supply and uptake of these substance, and crop residue with silicates/silicic acid can increase their concentration (Nolla et al., 2006) gradually in soil system. Upon dissolution, they produce SiO_3^{2-} , an electron acceptor. And, in most solutions at wide range of pH value, Si^{4+} is dissolved as a hydroxocomplex. $\text{Si}(\text{OH})_4$; is the formula that best represents the nature of the hydroxocomplex, but H_4SiO_4 (in silicic acid form) is commonly used to indicate that the complex can beat H^+ ions and thus, behave as an acid.

Based on the researches in Taiwan and US, 30% of silicic acid must be added to the degraded soil including with 10% of secondary nutrients, 20% of NPK minerals each in order to restore soil quality just like newly opened forest to increase productivity by 1 time as well as preventing plant diseases and insects.

(<http://www.h4sio4.co.th/index.php/2011-10-25-09-19-21.html>- retrieved 01 May 2016).

6.4.6 GWP: the combined Climatic Impact of CH₄ and N₂O emissions

Global warming potential (GWP) defined as a relative measure of how much heat a greenhouse gas traps in the atmosphere. It compares the amount of heat trapped by a certain mass of the gas in question to the amount of heat trapped by a similar mass of carbon dioxide (https://en.wikipedia.org/wiki/Global_warming_potential).

From the study, GWPs were calculated using IPCC factors (IPCC, 2001) to assess the combined climatic impacts from CH₄ and N₂O under various treatments factors as shown in Table (6.2).

The theory behind GWP estimation:

1. In GWP estimation, CO₂ is typically taken as reference gas, and an increment or reduction in emission of CH₄ and N₂O is converted into “CO₂-equivalent” by means of their GWPs.
2. The concept of global warming potential (GWP), one type of simplified index based on radiative properties, was introduced in order to estimate the potential future impacts of emissions of different gases upon the climate system in a relative sense (Lashof and Ahuja, 1990; Shine et al., 1990).
3. Recently, the net GWP has been estimated to complete understanding of agriculture’s impact on radiative forcing (Frolking et al., 2004; Yu et al., 2004; Robertson et al., 2000).

Based on the GWP, treatment with continuous oxygen supply showed significant reduction and without oxygen supply significant reduction of the net GWPs whether over a 20 years, or 500 years horizon. Meanwhile, for water level, shallow water (1:1) level greatly increased net GWPs than deep water (1:2) level. In addition, comparison of control (without calcium silicate addition) with addition of 1 t ha⁻¹ and 2 t ha⁻¹ of calcium silicate show significant ability to depress the net GWPs under both water level, with presence of continuous oxygen supply.

Overall, the lowest net GWPs were observed with 1 t ha⁻¹ calcium silicate treatment under both shallow and deep water levels without oxygen supply.

Therefore, addition of 1-1.5 t ha⁻¹ of calcium silicate was recommended as it will depress the net GWPs in both shallow or deep water level and either with or without oxygen supply condition.

Table 6.2 Net GWPs from CH₄ and N₂O emissions in rice paddies under different agricultural treatments ^a

Oxygen supplied	Water level	Calcium silicate (t ha ⁻¹)	CH ₄			N ₂ O			CH ₄ +N ₂ O		
			20 years	100 years	500 years	20 years	100 years	500 years	20 years	100 years	500 years
Yes	Shallow	0	4.13	1.53	0.46	317.96	342.24	180.37	322.09 ^a	343.77 ^a	180.83 ^a
Yes	Shallow	1	3.90	1.45	0.44	122.95	132.34	69.74	126.85 ^b	133.79 ^b	70.19 ^b
Yes	Shallow	2	4.07	1.51	0.46	157.61	169.65	89.41	161.69 ^{ab}	171.16 ^{ab}	89.87 ^{ab}
Yes	Shallow	3	4.31	1.60	0.48	223.48	240.55	126.77	227.80 ^{ab}	242.16 ^{ab}	127.26 ^{ab}
Yes	Deep	0	4.05	1.50	0.45	96.75	104.14	54.88	100.80 ^a	105.65 ^a	55.34 ^a
Yes	Deep	1	4.18	1.55	0.47	66.70	71.80	37.83	70.89 ^{ab}	73.35 ^{ab}	38.31 ^{ab}
Yes	Deep	2	4.00	1.49	0.45	32.09	34.54	18.20	36.10 ^b	36.03 ^b	18.65 ^b
Yes	Deep	3	4.17	1.55	0.47	42.88	46.16	24.32	47.06 ^{ab}	47.71 ^{ab}	24.80 ^{ab}
No	Shallow	0	20.18	7.49	2.27	19.35	20.84	10.98	39.54 ^a	28.33 ^a	13.26 ^a
No	Shallow	1	7.17	2.66	0.80	14.42	15.53	8.18	21.59 ^a	18.18 ^a	8.99 ^a
No	Shallow	2	8.19	3.04	0.92	20.40	21.96	11.57	28.59 ^a	25.00 ^a	12.49 ^a
No	Shallow	3	18.22	6.76	2.05	23.18	24.96	13.15	41.41 ^a	31.72 ^a	15.21 ^a
No	Deep	0	23.33	8.66	2.63	14.88	16.02	8.44	38.22 ^a	24.68 ^a	11.07 ^a
No	Deep	1	29.75	11.04	3.35	11.12	11.97	6.30	40.87 ^a	23.01 ^a	9.66 ^a
No	Deep	2	27.84	10.33	3.14	23.39	25.18	13.27	51.24 ^a	35.51 ^a	16.41 ^a
No	Deep	3	13.10	4.86	1.48	21.89	23.57	12.42	35.00 ^a	28.43 ^a	13.90 ^a

^a The IPCC GWPs factors (mass basis) for CH₄ and N₂O are 62, and 275 in the time horizon of 20 years, 23 and 296 in the time horizon of 100 years, and 7 and 156 in the time horizon of 500 years, respectively (IPCC, 2001). Means marked with the same letter for each agricultural treatments are not significantly different at $p < 0.05$ (Tukey's test)

6.5 Conclusion

Addition of calcium silicate showed different ability in mitigating methane, carbon dioxide and nitrous oxide emissions under shallow and deep water level with and/or without oxygen supply. For condition with oxygen, under shallow water level, 1 t ha^{-1} calcium silicate had significant efficacy reducing the net GWPs compared to untreated soil by 61.18%. On the other hand, under deep water level, 2 t ha^{-1} calcium silicate had significant ability reducing the net GWPs compared to untreated soil by 66.29% while for the condition without oxygen, addition of calcium silicate did not showed the significant ability in mitigating the net GWPs irrespective for both water levels. However, addition 1 t ha^{-1} calcium silicate showed the lowest net GWPs compared to other treatments for both shallow and deep water levels.

In addition, for cultivated soil, 2 t ha^{-1} calcium silicate had significant efficacy in mitigating nitrous oxide emission compared to 3 t ha^{-1} calcium silicate by 61%.

Chapter 7 General discussion

7.1 Summary of the study

A total of six studies have been conducted. The studies consist of soil incubation, rice cultivation on field trial and under glasshouse condition.

The first study was field trial. The objective was to access the performances and cost-effectiveness of various liming materials commonly used (ground magnesium limestone (GML), hydrated lime (HL), and liquid lime (LL)) to increase rice yield of acidic sulfate soil in Malaysia. Rice variety MR 219 was cultivated for two season and treatments used for this experiment were control (T1); 4 t ha⁻¹ ground magnesium limestone (GML) (T2); 2 t ha⁻¹ hydrated lime (T3); 20 L ha⁻¹ liquid lime applied only first season (T4); 20 L ha⁻¹ liquid lime applied both seasons (T5) and 2 t ha⁻¹ hydrated lime without fertilizer (T6). The treatment rate of GML (4 t ha⁻¹), hydrated lime (2 t ha⁻¹) and liquid lime (20 L ha⁻¹) were based on the common rate used by the farmers, as these rates were recommended rate by the Malaysian Government for rice production. Application of GML and hydrated lime increased rice yields for both season, in contrast to liquid lime application with no notable increase in rice yield on acidic sulfate soil. However, GML was a suitable liming material at the studied area (under acidic sulfate soil conditions). Application of 4 t ha⁻¹ year⁻¹ GML increased rice yield by 31.39%. Thus, the highest recorded rice yield was 8.05 t ha⁻¹ year⁻¹ with a calculated profit of USD 2156 compared to other treatments.

The second study was incubation study. The objective of this study was to evaluate the effect of GML to assess the possibility of reducing current application rate of 4 t ha⁻¹ commonly used by the farmers to improve the fertility of acidic sulfate soil in Malaysia. Reduction in liming materials means saving in material cost (lime) and labor. The acidic sulfate soil used in this experiment was incubated with 0, 2, 4 and 6 t ha⁻¹ GML under submerged condition. The soils were sampled and analyzed for selected chemical soil properties for every 30 days throughout incubation period of 120 days. The selected 120 days of incubation period correspond directly to the harvesting time of rice variety used, that is MR 219. From the study, application of 4 t ha⁻¹ GML were able to reduce exchangeable Al (< 2 cmol_c kg⁻¹), increase Ca (> 2 cmol_c kg⁻¹), Mg (> 1 cmol_c kg⁻¹), K (> 0.2 cmol_c kg⁻¹), available P (7-20 mg kg⁻¹) and Fe content (> 2 mg kg⁻¹), and similar effect were noted with application of 2 t ha⁻¹ GML. This indicates that the ameliorative effect of

2 t ha⁻¹ GML is similar to 4 t ha⁻¹ GML. Therefore, reduction in lime application from 4 t ha⁻¹ to 2 t ha⁻¹ is sufficient, promotes reduction in cost of GML by 50% from the common rate use by the farmers in Malaysia presently at 4 t ha⁻¹ GML.

The third study was incubation study. The objective was to evaluate the ameliorative effect of calcium silicate on acidic sulfate soil in Malaysia as an alternative soil ameliorant to GML. The acidic sulfate soil was incubated with 0, 1, 2, and 3 t ha⁻¹ of calcium silicate under submerged conditions. The soils were sampled every 30 days throughout the incubation period of 120 days. Application of calcium silicate induced a positive effect on soil pH and exchangeable Al; soil pH increased from 2.9 to 3.5, while exchangeable Al reduced from 4.26 to 0.82 cmol_c kg⁻¹, which is below the critical level of 2 cmol_c kg⁻¹ Al. Furthermore, the exchangeable Ca and Si contents in soil increased from 1.68 cmol_c kg⁻¹ to 4.94 cmol_c kg⁻¹ and from 21.21 mg kg⁻¹ to 81.71 mg kg⁻¹, respectively. Therefore, calcium silicate shows positive effect to alleviate Al toxicity in acidic sulfate soil (rice-cropped). Application of calcium silicate showed an ameliorative effect with increment in soil pH and nutrient supply capacity (for Ca and Si) in the soil.

The effects of GML and calcium silicate on acidic soil independently have been presented in study 2 and 3, respectively. Further, the fourth study was conducted to evaluate the integral effect of GML and calcium silicate on acidic sulfate soil 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 acidic sulfate soil. The acidic sulfate soils were incubated under submerged condition for 120 days with ground magnesium limestone (0, 2, 4, 6 t ha⁻¹) in-combination with calcium silicate (0, 1, 2, 3 t ha⁻¹). Data showed that, a total of 9 out of 16 combination rate met the desire 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. From the 9 combinations rate, only 2 combination rate (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 recommendations are, i) 2 t ha⁻¹ calcium silicate with 2 t ha⁻¹ GML cost USD 484 and, ii) 3 t ha⁻¹ calcium silicate with 2 t ha⁻¹ GML cost USD 559. The two combination rate were able to ameliorate the soil to the desired requirement of chemical

soil characteristics as stated above and reduce the liming material cost of rice-farmers in Malaysia under acidic sulfate soil.

The fifth study carries two (2) objectives. The first objective was to evaluate the efficacy of calcium silicate on GHG emissions under different water level with and/or without oxygen supplied of rice-cropped soil. The soil samples were incubated in the incubator for 840 hours at 25°C. The soil was incubated with 0, 1, 2 and 3 t ha⁻¹ of calcium silicate under two conditions. Condition one, different water level; (1:1, shallow) and (1: 2, deep) soil: water and further subjected to condition two; with oxygen and without oxygen supply. Control (untreated soil) was incorporated in the study as baseline condition (value). Addition of calcium silicate showed different ability in mitigating methane, carbon dioxide and nitrous oxide emissions under shallow and deep water level with and/or without oxygen supply. For condition with oxygen supplied, 1 and 2 t ha⁻¹ calcium silicate had significant efficacy in mitigating the net GWPs under shallow water level by 61.18% and under deep water level by 66.29%, respectively compared to the untreated soil. On the other hand, for condition without oxygen supplied, calcium silicate had no significant ability in mitigating the net GWPs. However, addition of 1 t ha⁻¹ calcium silicate gave the lowest net GWPs under both shallow and deep water level compared to other treatments.

Subsequently, the second objective was to determine the ability of calcium silicate on the N₂O emission of the cultivated rice. The treatments used were 0, 1, 2, 3 t ha⁻¹ of calcium silicate including bare soil with 3 replications. The Takanari rice variety was used. Emission of N₂O was sampled from seeding until harvest with interval of 7 days. The results showed that applications of calcium silicate stimulate the N₂O emission to a certain extent. However, soil treated with 2 t ha⁻¹ calcium silicate, significantly depressed N₂O emissions compared to soil treated with 3 t ha⁻¹ calcium silicate by 61%.

7.2 Overall conclusions

Acidic sulfate soils have limitations for good crop growth, and one of the potential method to improve the limitations are with application of liming materials. Liming materials such as ground magnesium lime, hydrated lime and liquid lime is a common practice by rice-farmers in Malaysia under the acidic sulfate soil condition. Among these materials, GML shows the most potential. GML were able to improve rice yield by 31.39% with 4 t ha⁻¹ GML as noted in Chapter 2. However, with 4 t ha⁻¹ GML, cost becomes an issue.

Cost incurred to apply soil amendments especially liming materials needs to be taken into consideration. Table 7.1 shows the feasibility analysis of the different liming materials inclusive of labor cost. The selected amendments were based on study data from Chapter 3, 5 and 6. Currently, farmers are using GML at rate of 4 t ha⁻¹ in Malaysia with the cost of USD 668 for rice cultivation. However, in Chapter 3, data indicates that with reduced rate of GML at 2 t ha⁻¹, achieved desired soil characteristics value for exchangeable Al < 2 cmol_c kg⁻¹, Ca > 2 cmol_c kg⁻¹, Mg > 1 cmol_c kg⁻¹, K > 0.2 cmol_c kg⁻¹, available P in the ranged of 7-20 mg kg⁻¹ and Fe content > 2 mg kg⁻¹ on the acidic sulfate soil for good increase in rice growth. Thus, it is possible to reduce the GML from 4 t ha⁻¹ (common rate) to 50% less with only 2 t ha⁻¹. With that, if farmers choose to apply only 2 t ha⁻¹ GML, the cost of GML directly reduced 50%. Besides GML, we also investigate the ability of calcium silicate as an alternative amendment on the acidic sulfate soil in Chapter 4, and results showed that, calcium silicate can also be an alternative soil amendment. Calcium silicate decreased Al toxicity, supply sufficient amount of Ca and Si needed for rice cultivation. Thus, if farmers choose to apply calcium silicate alone, it would cost about USD 75 (1 t ha⁻¹), with maximum rate of 3 t ha⁻¹ (USD 225).

Stands alone effect of GML and calcium silicate were positive on acidic sulfate soil, and followed with study on integral effect of GML with calcium silicate in Chapter 5, in-combination of both amendments. The effective rates of the combinations were evaluated based on the 30th days of incubation; timeline that is sufficient to note changes in soil chemical characteristics (i-v) as highlighted below to achieve good rice growth.

- i) pH > 4 (Shamshuddin, 2006)
- ii) Al < 2 cmol_c kg⁻¹ (Hiradate et al., 2007)
- iii) Ca > 2 cmol_c kg⁻¹ (Palhares de Melo et al., 2001)
- iv) Mg > 1 cmol_c kg⁻¹ (Dobermann and Fairhurst, 2000)
- v) Si content > 43 mg kg⁻¹ (Narayanaswamy and Prakash, 2009)

The reason for selection of 30th days of incubation because the acidity gradually decrease in soil and water which will support positive crop growth in-line with vegetative, reproductive and flowering of rice growth phases. In addition, it is more practical and applicable by the local farmers compared to 60D, 90D or 120D because 30D is more time-suitable for them otherwise they need to wait too long before they start planting. Through the studies, obtained optimal combinations of calcium silicate and GML to reduce the cost from the common practice now in Malaysia. As a result, there are 2 possible combination rate, which are i) 2 t ha⁻¹ GML with 2 t ha⁻¹ calcium silicate cost at USD 484 and, ii) 2 t ha⁻¹ GML with 3 t ha⁻¹ calcium silicate cost at USD 559.

Besides the positive effect on the soil chemical characteristics, efficacy of calcium silicate has been evaluated in mitigating the GHG emissions of rice cropped soil in Chapter 6. As a result, under the condition of oxygen supplied, addition of 1 and 2 t ha⁻¹ calcium silicate had significant ability reducing the net GWPs by 61.18% and 66.29% compared to untreated soil under shallow and deep water levels, respectively. On the other hand, under the condition without oxygen supplied, addition of 1 t ha⁻¹ calcium silicate gave the lowest value of net GWPs in both shallow and deep water levels. In addition, 2 t ha⁻¹ calcium silicate has significant efficacy in reducing the nitrous oxide emissions by 66% compared to 3 t ha⁻¹ calcium silicate from the rice cultivated soil. In other word, it means that addition of calcium silicate at higher amount would improve the soil to the desired level (soil chemical characteristics), but it has low ability in mitigating the GHG emissions and also it will cost more to the farmers.

Finally, from this study, addition of GML in-combination with calcium silicate was able to alleviate the soil acidity of acidic sulfate soil. Addition (in-combination) of calcium silicate with GML have two benefits which are, i) as soil ameliorative to improve soil chemical characteristics of acidic sulfate soil and, ii) ability to mitigate the net GWPs. In addition to that, industrial by-product such as calcium silicate slag that treated as waste in Malaysia can be recycled; this add value to the whole industry and agriculture sector in Malaysia.

Table 7.1
Cost of the selected soil amendments

No	Soil amendments	Cost (USD)	Justification
1	4 t ha ⁻¹ GML	668	Common practice in Malaysia
2	2 t ha ⁻¹ GML	334	Show possibility in reducing the rate from common practice.
3	2 t ha ⁻¹ GML + 2 t ha ⁻¹ SSF	484	Achieved the recommended level of all the targeted soil chemical characteristics except soil pH
4	2 t ha ⁻¹ GML + 3 t ha ⁻¹ SSF	559	Achieved the recommendation levels of all the targeted soil chemical characteristics
5	1 t ha ⁻¹ SSF	75	Significantly reduced the net GWPs under shallow water level with presence of oxygen
6	2 t ha ⁻¹ SSF	150	Significantly reduced the net GWPs under deep water level with oxygen supplied
7	1 t ha ⁻¹ SSF	75	Lowest net GWPs value under shallow and deep water levels without oxygen supplied
8	2 t ha ⁻¹ SSF	150	Significantly reduced N ₂ O emission by 66% compared to 3 t ha ⁻¹ SSF

GML- ground magnesium limestone

SSF- silicate slag fertilizer

7.3 Future research prospects

Application of calcium silicate was able to alleviate the soil acidity and shows the potential ability to reduce GHG emission of rice-cropped soil. Therefore, the author reckons the potential use of calcium silicate slag as soil amendment. Stated below are the recommendations for future research on calcium silicate slag.

1. Field scale study of rice cultivation with application of calcium silicate slag on acidic soil to evaluate the *in-situ* effect of the soil, rice yield and also GHG emissions.
2. Role of silicate as electron acceptor to accelerate and/or inhibit N₂O emission through nitrification or denitrification.
3. Sustainability and the movement of the calcium silicate in soil. From this study, the results showed that calcium silicate independently can be an alternative soil amendment on reducing toxicity of soil. Besides reducing soil toxicity, addition of calcium silicate in-combination with GML showed better improvement of soil fertility. However, less study on the movement of the calcium silicate through the soil are available. From their movement studies, we could know the sustainability of the calcium silicate applied on agriculture soil. Hence, we could further assess their suitable rate and how frequently do farmers need to apply on their soil prior rice planting. This could help farmers a lot especially on reducing their input cost and increase their disposable income.
4. Further search for other sources of silicate from industry. As such, iron slag which also comes from industrial by-product. By utilizing industrial by-product, human can reduce the industrial waste, and often industrial wastes are cheaper (economical). However, preliminary studies of their potentials and effects need to be conducted in a controlled and/or laboratory environment.

5. Method of calcium silicate slag application; Split application- Soil amendments only applied one (1) time a day before the soil was incubated to study on its ability on acidic soil and also on reducing GHG emission. From the data produced, it could be used further to increase its efficiency. One of the alternative options is split application method. Calcium silicate could be applied more than one (1) time throughout rice cultivation. For example, first application can be done before rice planting and the next application could be done during reproductive stage because other researcher found that emission of GHG was increased during early flowering due to activity of rice plants which provide soil bacteria with organic root exudate or root litter

6. Study on calcium silicate slag as slow release fertilizer.

7. Calcium silicate slag application on other crops and agricultural soils.

8. Groundwater leaches effects; even though acidic soil could be ameliorated by using several amendments, less attention have been given to the environmental impact. The effect of the groundwater, whether it is contaminated with heavy metal which later it would effect on human or aquatic life.

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