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### **Review** Article

## Formation and Utilisation of Acid Sulfate Soils in Southeast Asia for Sustainable Rice Cultivation

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### ABSTRACT

Large parts of lowland areas in Southeast Asia were submerged in seawater some 4300 years ago due to a rise in sea level. During this period, the coastal plains in the region were pyritised. Agricultural development led to oxidisation of the pyrite (FeS<sub>2</sub>) which in turn allowed weathered mineral silicates to be present in the sediments. High levels of Al and/or Fe are thus present in the soils/water that affect plants and aquatic life. Rice grown on the so-called acid sulfate soils suffer from low pH and Al<sup>3+</sup> and/or Fe<sup>2+</sup> toxicity, with yields below the national average. The critical pH and Al concentration for rice growth is 6 and 15-30 uM respectively. The soil become infertile due to high concentrations of acid sulfate . Application of ground magnesium limestone (GML) or basalt in combination with bio-fertiliser fortified with phosphate-solubilising bacteria (PSB) can help reduce the acid sulfate. The PSB not only excrete organic acids that inactivate Al and Fe via chelation, but also increase soil pH to the level that precipitates Al as inert Al-hydroxides. Additionally, rice roots are able to excrete organic acids under the presence of high concentration of Al and/or Fe, which further reduces the availability of Al and Fe in the water.

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#### **INTRODUCTION**

#### **Definition and occurrence**

Acid sulfate soils contain pyrite (FeS<sub>2</sub>), occurring under submerged conditions. Immediately above the pyritic layer is

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usually the sulfuric horizon. According to Soil Survey Staff (2014), sulfuric horizon is defined by the presence of:

- Mineral jarosite[(KFe<sub>3</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>]; and
- 2. More than 0.05% water-soluble sulfate.

The soils, taxonomically classified as Sulfaquents and Sulfaquepts, are sporadically distributed throughout the lowland coastal plains of Southeast Asia. The global occurrence of acid sulfate soils is not related in any way to climatic conditions or the mineralogical properties of the coastal sediments from which they are formed. In Southeast Asia, the soils are found in the Mekong Delta, Vietnam (Husson et al., 2000), Bangkok Plains, Thailand (van Breemen, 1976), Kalimantan, Indonesia (Anda et al., 2009) and Kedah-Perlis Plains, Malaysia (Azmi, 1982; Shamshuddin, 2006). Department of Agriculture estimated about 0.4 million ha of acid sulfate soils in Peninsular Malaysia alone (Figure 1).

Being related to the sea, pyrite-bearing sediments usually occur along the coastal plains throughout Southeast Asia. The areas where these sediments occur are in mangrove swamps, having big and small organisms, living harmoniously side by side. The areas become natural habitat for fish and crabs that co-exist with the forest species. After the areas were opened up to make way for agricultural development, soil acidity and Al and/or Fe toxicity became serious threats to crops and aquatic life



*Figure 1.* A map of Peninsular Malaysia showing the distribution of acid sulfate soils (Green = Kranji Series; Purple = Sedu-Parit-Botak Associations; Red = Telok- Guar Associations)

*Source*. Modified from Department of Agriculture, Peninsular Malaysia

(Shamshuddin, 2006). Thus, special soil management practices are necessary to sustain crop production (Shamshuddin, 2006; Shamshuddin et al., 2014).

Acid sulfate soils in Southeast Asia have been extensively studied (van Breemen, 1976; Shamshuddin & Auxtero, 1991; Husson et al., 2000; Shamshuddin, 2006; Anda et al., 2009; Shamshuddin et al., 2014). Major characteristics of the soils are as follows:

- 1. Pyrite occurs in the sediments under submerged conditions;
- Jarosite is formed on oxidation of this pyrite;
- Simultaneous release of soil acidity into the environment, resulting in soil pH < 3.5;</li>

- Silicates in the soils dissolve to release Al and/or Fe into the soils;
- 5. The amount of Ca and Mg in the soils are insufficient for crop growth; and
- P-deficiency is common in acid sulfate soils due to its fixation by Al and/or Fe.

#### Utilisation for rice cultivation

There is an increased need for land in Southeast Asia to cultivate crops in order to meet the ever-increasing demand for food and fibre. As such, the infertile acid sulfate soils can be put to good use, especially for food production. Studies were carried out to protect the soil for rice (Azura et al., 2014), oil palm (Auxtero and Shamshuddin, 1991) and cocoa cultivation (Chew et al., 1984; Shamshuddin et al., 2004b). Malaysia needs to increase its rice self-sufficiency level (SSL) from the current 70% to >80% by 2020. However, the country faces difficulties to achieve the set target due to various constraints: 1) Land allocated for rice cultivation is decreasing because paddy fields are being converted to other land uses; and 2) Soil and crop productivity has remained stagnant due to lack of investment on innovative agronomic research.

Agricultural activity is a nutrient mining process; hence, the soil needs to be replenished regularly with plant nutrients. In Peninsular Malaysia, some of the paddy soils adjacent to acid sulfate soils are chemically degraded (Shamshuddin, 2006). The areas in question are in Kedah-Perlis Plains (Azmi, 1982) and Kemasin-Semerak Integrated Agricultural Development Project, Kelantan (Enio et al., 2011). However, they have the potential of becoming good agricultural land if proper agronomic procedures are put in place.

Rice grown on acid sulfate soils produces yield of about 2 t ha<sup>-1</sup> season<sup>-1</sup> (Elisa et al., 2012; Elisa et al., 2014), which is far below the national average of 3.8 t ha<sup>-1</sup> season<sup>-1</sup>. If we can increase the yield to a level above 5 t ha<sup>-1</sup> season<sup>-1</sup>, farmers growing rice in the affected areas can make a decent living. This is not to mention the increased rice stock in the country, leading to increase in rice SSL.

The root causes of low rice yield are: 1) Acid sulfate soils contain too much acidity; 2) rice planted on the soils are subjected to Al and/or Fe stress; and 3) the availability of P is low due to fixation by Al and/or Fe prevalent in the soils. Infertility is due oxidation of pyrite in the sediments. When the hydromorphic areas are drained, the pyrite is exposed to the atmospheric conditions and subsequently oxidised, resulting in the release of high amount of acidity (Shamshuddin et al., 2004a; Shamshuddin, 2006). A new mineral known as jarosite [KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] is formed in the end. Under acidic conditions, mineral silicates present in the sediments undergo weathering that result in the release of high amount of Al and/or Fe into the environment which can be toxic. The presence of these acidic metals in the paddy fields can also reduce the availability of P for the uptake by rice.

The pH of water in many of the paddy fields located on acid sulfate soils is 3-4, which is far below the critical pH of 6 needed for the healthy growth of common rice varieties in Malaysia (Azura et al., 2011; Shamshudin et al., 2013; Shamshuddin et al., 2014; Alia et al., 2015). According to Rosilawati et al. (2014) and Azura et al. (2014), soil pH can be increased to the required level for rice cultivation by applying GML or hydrated lime. An alternative method is to apply ground basalt (Panhwar et al., 2014a). Basalt is better than GML in terms of its ameliorative effects as it not only increases soil pH and supplies Ca and Mg, but also supplies K and P (Shazana et al., 2013). Besides, basalt releases Si which improves crop growth, leading to prevention of disease that affect yield, such as rice blast.

Panhwar et al. (2014b) identified three phosphate-solubilising bacteria (PSB) that existed in acid sulfate soils in Malaysia. These PSB have the potential to be effective microorganisms for the formulation of a biofertiliser for rice cultivation on acid sulfate soils. These special microbes are not only able to make P more available to rice plants in the fields than otherwise are, they can also excrete organic acids that can reduce Al and/ or Fe in the water of the paddy fields via the process of chelation. As such, the rice plants will grow under less stress of Al and/or Fe. Besides, the PSB release a certain chemical that increases water pH to a level above 5 (Panhwar et al., 2014b). The increase in pH would precipitate Al as inert Al-hydroxides, thus further reducing the availability of Al

(Shamshuddin et al., 2013; Shamshuddin et al., 2014). Acid sulfate soils will continue to be utilised for rice cultivation in the future given the scarcity of fertile agricultural land in Southeast Asia. The objectives of this paper are: 1) to discuss in detail the formation of acid sulfate soils in Southeast Asia; and 2) to explain how these soils are managed using innovative agronomic practices for sustainable rice cultivation.

### PYRITISATION OF THE COASTAL SEDIMENTS IN SOUTHEAST ASIA

## Sea level rise in Southeast Asia during the Holocene

Climate change is a global phenomenon, naturally occurring intermittently throughout geological time, with or without human intervention. During the Last Glacial Maximum, some 20,000 years ago, a vast land area was formed in Southeast Asia (Tjia, 2012) that determined the present landscape and geological style of the region (Figure 2). Global ice melts slowly



*Figure 2.* A map of Southeast Asia showing the countries in the region *Source.* Geological Society of Malaysia

thereafter, rising the sea level 15 mm year<sup>1</sup>. In Southeast Asia, it reached the maximum elevation of 5 m above the present about 4,300 years before present (Tjia et al., 1977; Tjia, 2012).

It was during this period that the lowlying areas in the coastal plains of Southeast Asia were inundated with seawater for a long period of time. Thus, the land area was smaller than it is today. The sediments were pyritised. The phenomenon was proven by a study conducted in the Kelantan Plains, Malaysia (Enio et al., 2011). Using the distribution of pyrite in the sediments, researchers were able to predict the coastline in the plains at the height of the sea level rise during the Holocene (Fig. 3). Similar phenomenon would have occurred in the Bangkok Plains (Thailand), Mekong Delta (Vietnam) and Kalimantan (Indonesia).

### The mineralisation of pyrite

Figure 4 shows the mineralisation of pyrite in the coastal sediments in Southeast Asia. The process requires the presence of  $SO_4^{2-}$ , supplied by seawater. This sulfate ion goes into the sediments during high tide. Iron required for the pyritisation process is naturally present in the sediments. Under anaerobic condition, both ions undergo reduction process, expedited by the microorganisms living naturally in the sediments:

1. 
$$SO_4^2 \rightarrow S^2$$
  
2  $Fe^{3+} \rightarrow Fe^2$ 



*Figure 3.* A map showing the predicted coastline in the Kelantan Plains, Malaysia when the sea level was 5 m above the present

Source. Adapted from Enio et al. (2011)



*Figure 4.* Mineralisation of pyrite in the coastal sediments *Source.* Adapted from Shamshuddin (2014)

Eventually, the Fe<sup>2+</sup> and S<sup>2-</sup> will react to form FeS<sub>2</sub>, the so-called pyrite. The overall reaction as described by Pons et al. (1982) is as follows:

$$Fe_2O_3 + 4SO_4^2 + 8CH_2O + \frac{1}{2}O_2 \rightarrow 2FeS_2 + 8HCO_3 + 4H_2O$$

This process continues uninterrupted until sulfate is no longer available for the reaction, that is after the seawater recedes. The pyrite so formed remains stable in the sediments provided that it is under submerged condition. Pyrite shown in Figure 3 can be found in the sediments some distance away from the present coastline (Shamshuddin, 2006; Enio et al., 2011). Shamshuddin (2006) reported that some coastal sediments in Peninsular Malaysia contained up to 2-3% pyrite, resulting from thousands of years of pyritisation process.

Pyrite exists in the form of cubic crystal (Figure 5). To get the crystals seen in Figure 5, the soil sample containing pyrite has to be freeze-dried immediately before it is treated

*Figure 5.* SEM micrograph of pyrite found in the coastal sediments of Malaysia *Source.* Shamshuddin et al. (2004a)

for observation under scanning electron microscope. Otherwise, it will undergo immediate oxidation to form yellowish jarosite.

Soil profile containing pyrite occurring under reducing condition looks bluish, indicative of its origin and/or relation with the sea. Figure 6 is a picture of a freshly dug profile of Kranji Series (Sulfaquent) located close to the sea in Peninsular Malaysia (Shamshuddin, 2014). Noordin (1980) studied acid sulfate soils found in Perak and his findings showed the presence of diatoms in the coastal sediments containing pyrite; diatoms are living creatures that thrive in the seabed. This finding has proven beyond doubt that for pyritisation process to occur, seawater is required to supply the required  $SO_4^{2-}$  ions.



*Figure 6.* A profile of an acid sulfate soil found in Peninsular Malaysia *Source:* Shamshuddin (2014)

## OXIDATION OF PYRITE UNDER AEROBIC CONDITION

Under flooded environment, pyrite is known to be stable, causing harm to living

creatures in the sediments, either plants or animals. Its crystal structure remains intact until aerobic condition sets in due to drop in water table. When this happens, the pyrite undergoes oxidation and/or disintegration that releases acidity to the soil environment (Shamshuddin, 2006).

Soil containing pyrite in Southeast Asia are usually drained and opened up for the cultivation of rice. In Malaysia, to prevent seawater from entering the land, a specially designed bund is constructed (Figure 7). The excess water is then removed by digging drains at appropriate size and depth. The water table in the soils of the areas drops and subsequently the pyrite is exposed to the atmospheric conditions, resulting in the disintegration/dissolution. This process releases a lot of acidity to the environment, with pH decreasing to the level below 3.5 (Shamshuddin and Auxtero, 1991; Shamshuddin et al., 2004a).

The reaction can be formulated as follows (van Breemen, 1976):



Further oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> leads to the generation of more acidity:

$$2Fe^{2+}(aq) + \frac{1}{2} O_2(aq, g) + H_2O \rightarrow Fe_2O_3(s) + 4 H^+(aq)$$

Reaction 1 shows a lot of acidity is being produced with concomitant formation of the yellowish jarosite (Figure 7). Jarosite is a stable mineral and thus, remains a long time in the soil. However, under extreme weathering condition, the jarosite can further be oxidised to reddish hematite as shown by Reaction 2.

The first sign of pyrite disintegration in the soils is etching of the crystals (Figure 8). Finally, the pyrite crystals are completely disintegrated, with the formation of jarosite soon thereafter (Shamshuddin & Auxtero, 1991; Shamshuddin et al., 2004a).



*Figure 7.* Oxidation of pyrite on exposure to the atmospheric conditions *Source.* Adapted from Shamshuddin (2014)



*Figure 8*. SEM micrograph showing pyrite undergoing oxidation *Source*. Shamshuddin et al. (2004a)

Yellowish jarosite mottles can be clearly seen in the sulfuric horizon of acid sulfate soils (Figure 9). In between the yellowish mineral, there are spots of reddish materials so named hematite. Jarosite is partly converted to hematite if extreme weathering condition occurs persistently in the area for a long period of time.

### **GENERATION OF SOIL ACIDITY**

Pyrite, on exposure to the atmospheric conditions, undergoes immediate oxidation, generating a lot of acidity with pH at < 3.5 (van Breemen, 1976; Shamshuddin and Auxtero, 1991; Shamshuddin et al., 2014). The pH of water in the vicinity of acid sulfate soils area is likely to be < 4 (Shamshuddin, 2006; Azura et al., 2011; 2012). The low pH contributes to the enhanced weathering of mineral silicates present in the sediments. In the end, large amounts of Al and/or Fe are released into the soil environment, affecting plant growth and aquatic life in the vicinity of acid sulfate soils.



*Figure 9.* A picture showing yellowish jarosite occurring in the topsoil of the Kelantan Plains *Source.* Shamshuddin (2006)

The pKa of Al is 5. When water pH goes down below this level, Al in the water undergoes immediate hydrolysis, releasing more acidity to the environment. This further chemically aggravates the acid sulfate soils. The hydrolysis reaction is described by the following equation:

$$Al^{3+}.6H_2O + H_2O \rightarrow Al^{2+}OH.5H_2O + H_3O^+$$

When water pH goes up above 5, Al begins to precipitate as inert Al-hydroxides  $[Al(OH)_3]$ , which is no longer toxic to rice plants.

Fe, with pKa of 3, undergoes immediate hydrolysis in the same manner as that of Al, but more vigorously, with protons being released as shown below:

$$\begin{array}{rcl} \mathrm{F}e^{3+}.6\mathrm{H}_{2}\mathrm{O} + \mathrm{H}_{2}\mathrm{O} & \rightarrow & \mathrm{F}e^{2+}\mathrm{OH}.5\mathrm{H}_{2}\mathrm{O} \\ + & \mathrm{H}_{3}\mathrm{O}^{+} \end{array}$$

As such, both elements are regarded as acidic metals, with Fe being more acidic than that of Al. If both metals are present in high amounts in the water of the paddy fields on acid sulfate soils, the pH will be in equilibrium at 3-4 (Azura et al., 2011, Shamshuddin et al., 2013; Shamshuddin et al., 2014). The concentration of Al in the water can reach up to 800  $\mu$ M (Shamshuddin et al., 2014). Both low pH and high Al concentration will certainly affect the growth of rice plants eventually affecting their yield. Like Al, Fe starts to precipitate as Fe-hydroxides [Fe(OH)<sub>3</sub>] when pH is above its pKa value. So, to reduce the effects

of Fe toxicity, we only need to increase soil pH to about 4.

#### EFFECTS OF pH, AI AND Fe TOXICITY ON RICE

#### Effects of pH

In normal soils with water pH about 6, rice roots grow without limitation. Figure 10(a) shows the morphology of a rice root growing at pH about 6, without H<sup>+</sup> stress. There are many root hairs; hence, the roots are able to absorb sufficient amounts of nutrients required by rice for its growth. On the other hand, at pH below 3.5, rice root grows abnormally. When water pH is about 3, its growth is severely stunted due to absence of root hairs (Figure 10(b)). This could be the scenario when rice is grown on acid sulfate soils without undergoing amelioration. Under field condition, the pH of water is < 4 (Elisa et al., 2011; Shamshuddin et al., 2014). Worse still, the pH of water in some paddy fields on the chemically degraded acid sulfate soils in the country is 3 or less. Without alleviating the soils using the state-of-the-art agronomic practices, the areas are not suitable for rice cultivation like parts of Kemasin-Semerak Integrated Agricultural Development Project (IADP), Kelantan (Figure 3) where some farmers have abandoned the tradition of growing rice to support their livelihood.

### **Effects of Al**

Rice growing without the presence of Al in the water of their paddy fields is healthy. This is because the cells in its roots are able to function normally. Figure 10(c) shows the structure of the cells in the root of rice



*Figure 10*. Rice root growing under different pH: (a) & (b) at high pH [6.0]; (c) & (d) at low pH [3.0] *Source*. Alia et al. (2015)

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plant in the absence of Al. It is seen that the cellular structures of the roots are perfectly normal and healthy. In the presence of high concentrations of Al, rice plants grow under stress, affecting the growth of their root cells; the root cells are damaged severely by Al toxicity as shown in Figure 10(d). The damaged root cells will not be able to absorb sufficient amounts of nutrients; hence, the growth of rice is severely affected.

Under field condition, the concentration of Al is more than 800 µM (Shamshuddin et al., 2013; Shamshuddin et al., 2014). This level is far above the critical Al concentration for the rice growth of 15-30 µM (Azura et al., 2011; Alia et al., 2015). It is clear that the condition is not suitable for rice cultivation unless the soils are treated with appropriate amendments to raise the pH to a sufficient level to precipitate the Al as inert Al-hydroxides. Most of the Al is removed from the water when pH is about 5.2. However, to raise pH of acid sulfate soils to this level is costly (Rosilawati et al., 2013; Azura et al., 2011). We found that it is good enough if the water pH is about 4.5 because rice has a built-in mechanism to protect itself against Al toxicity (Shamshuddin et al., 2013; Shamshuddin et al., 2014; Alia et al., 2015).

### **Effects of Fe**

Rice is also affected by Fe stress. Like Al, the presence of excess amount of Fe in the water reduces rice growth significantly. Iron in the form of  $Fe^{2+}$  is toxic to rice plants (Shamshuddin et al., 2013; Shamshuddin et al., 2014; Alia et al., 2015). It was found that excessive amount of Fe was present in the acid sulfate soils of the Kelantan Plains, indicated by the red colour of the water in the paddy fields (Shamshuddin, 2006). When the paddy fields in the area are flooded during the growing season, the water in the paddy fields will look reddish in colour, indicative of the presence of high amount of Fe(OH)<sub>3</sub> (Figure 11).

Within two weeks, high amount of  $Fe^{2+}$ ions would be produced by reduction of  $Fe^{3+}$ . According to Muhrizal et al. (2003), this reduction is expedited by the presence of high quality organic matter. The reaction taking place in the water is described using the following equation (Konsten et al., 1994; Muhrizal et al., 2006):

$$Fe(OH)_3 + \frac{1}{4}CH_2O + 2H^+ \rightarrow Fe^{2+} + \frac{1}{4}CO_2 + \frac{11}{4}H_2O$$

During the reduction process, protons are consumed, resulting in a slight pH increase. Unfortunately, this mechanism can only increase water pH to about 4, which is



*Figure 11.* Flooded rice fields in the Kelantan Plains containing Fe-hydroxides *Source.* Shamshuddin (2006)

inadequate to precipitate all Al present in the water. We can, however, reduce the effects of toxicity resulting from  $Fe^{2+}$  by expediting the reduction process so that the period for the roots exposed to the adverse condition is significantly shortened (Shamshuddin, 2006). This can be achieved by applying organic matter at the appropriate rate (Muhrizal et al., 2003).

### THE MECHANISMS OF RICE TOLERANCE TO AI AND/OR Fe TOXICITY

If the concentration of Al in the water is not too high, rice can withstand stress induced by the former, which is achieved via a special mechanism. An experiment was carried out in the laboratory at Universiti Putra Malaysia, Serdang to determine the mechanism of Al tolerance using rice seedling variety MR 219, the most popular variety grown in Peninsular Malaysia. In this experiment, rice seedlings were subjected to the stress of various Al concentrations. Organic acids secreted by the roots of the seedlings were determined. The results of the experiment are shown in Figure 12.

As the concentration of Al increased, the amount of organic acids secreted also increased. The critical level of the Al concentration is 15-30  $\mu$ M (Shamshuddin, 2014), which is consistent with the critical Al concentration determined by Alia et al. (2015). Below this level of Al concentration, the amount of organic acids secreted is negligible. It means that if the concentration



*Figure 12.* Excretion of organic acids by rice roots (a) in the presence of Al; (b) in the presence of Fe *Source.* Adapted from Alia et al. (2015

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of Al is less than 30  $\mu$ M, the rice seedlings are not affected significantly by Al stress. In reality, organic acids in this experiment were secreted in response to Al stress. Among the organic acids released by the roots, malic acid was secreted the most while citric acid was the least (Figure 12(a)). Hence, it is believed that malic acid plays an important role in rice tolerance to Al toxicity. Like Al, rice roots respond to Fe stress by secreting organic acids (Figure 12(b)). However, the most important organic acid secreted by the rice roots due to Fe stress was citric acid, followed by citric acid. The least amount of organic acid released was malic acid.

How organic acids help rice defend itself against Al toxicity. The same mechanism can be used to explain its tolerance to Fe toxicity. The surface of rice root is negatively-charged; hence, the positivelycharged Al is naturally attracted to it (Shamshuddin et al., 2013; Shamshuddin, 2014; Shamshuddin et al., 2014). As soon as the Al touches the root surface, the root



*Figure 13.* The process of Al chelation by organic acids at the Al-root interface *Source.* Adapted from Shamshuddin et al. (2014)

responds by secreting organic acids. The organic acids then start to chelate the Al, making it inactive (Figure 13). The chelated Al and/or Fe, located at the root-water interface, are not toxic to rice plants. In this way, rice plants are able to grow normally, giving good yields.

Structure of a plausible organic acid involved in the chelation of Al and/or Fe is shown in Figure 14. The Al and/or Fe chelated by the organic acid remain stable until they are degraded by the actions of microbes living in the soils.



*Figure 14.* The pictorial representation of Al and/or Fe chelated by an organic acid *Source.* Adapted from Shamshuddin (2014)

#### ALLEVIATION OF SOIL INFERTILITY FOR RICE CULTIVATION

# Effects of amendment application on soil pH

A study was conducted in glasshouse in Malaysia to determine the effect of applying various amendments on soil pH (Figure 15). Soil pH of the control treatment did not change significantly, remaining



*Figure 15.* Effect of applying various amendments on soil pH

below 4. However, the pH of the ground basalt treatment increased slightly after 90 days of application. In contrast, GML treatment increased soil pH to a value above 5. The slight pH increase due to basalt treatment can be explained by its low rate of disintegration/dissolution (Shazana et al., 2013). The best treatment in this study was GML in combination with bio-fertiliser.

## Effects of applying GML on the growth of rice

Liming acid sulfate soils using GML for rice production is a standard practice in Malaysia (Shamshuddin, 2006). GML reacts with the soil within a short time, increasing soil pH to the level depending on the amount applied. Lime requirement of acid sulfate soils to raise soil pH to a value above 5 is 6 t GML ha<sup>-1</sup> (Rozilawati et al., 2013), but this rate of application is too costly for farmers in Southeast Asia. The recommended liming rate for acid sulfate soils in Malaysia is 4 t ha<sup>-1</sup> although soil pH remains below 5 (Shamshuddin, 2006). When GML is applied, the following reactions take place:

$$CaMg (CO_3)_2 + H_2O \rightarrow Ca^{2+} + Mg^{2-}$$
$$+ 2CO_3^{2-}$$
$$CO_3^{2-} + H_2O \rightarrow HCO_3^{-} + OH^{-}$$

The hydroxyl ions would then react with the Al in the solution to be precipitated as Al-hydroxides, which over time may be crystallised to form gibbsite [Al(OH)<sub>3</sub>]:

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

The GML application not only increases soil pH that remove Al from the solution, but also supplies significant amount of Ca and Mg, which are needed in high amount in the rice fields (Shamshuddin, 2006; Panhwar et al., 2014a). Without GML application, rice plants are affected by low pH and/ or Al toxicity and hence their growth are severely stunted (Figure 16(a)). Here it is seen that the rice leaves are brownish in colour, indicative of Al toxicity. The poor rice growth could also be due to insufficient amount of Ca and/or Mg in the soil.

Fortunately, if 4 t GML ha<sup>-1</sup> is applied onto the soil, rice grows normally (Figure 16(b)). Due to GML treatment, soil pH is increased to the level good enough for the growth of rice. Although soil pH was below 5 with substantial amount of Al present in the water, the plants were able to grow well because they the ability to secrete organic acids that reduce Al toxicity (Shamshuddin et al., 2013; Shamshuddin et al., 2014; Alia et al., 2015). J. Shamshuddin, Q. A. Panhwar, F. J. Alia, M. A. R. S. Shazana, O. Radziah and C. I. Fauziah



*Figure 16.* Rice grown on acid sulfate soil (a) Control treatment; (b) Soil amended by GML *Source.* Azura et al. (2014)

## Effects of applying basalt on the growth of rice

Basalt application is a good long-term solution to treat infertility of acid sulfate soils in Southeast Asia. The reason being it takes time for basalt to disintegrate and dissolve completely in the soil although under low pH condition (Shazana et al., 2013). But once dissolved, it not only increases soil pH significantly and subsequently supplies Ca and Mg, but also improves soil fertility by releasing K and P which are also needed in high amounts by rice plants (Panhwar et al., 2014a). It means that basalt application slightly reduces the cost of rice production because it can cut down the application of K- and P-fertiliser. The only problem is that its ameliorative effects take a long time to be realised. However, basalt dissolution releases Si, an essential element for rice growth. With its uptake, rice plant appears to be healthier and consequently able to prevent the outbreak of rice blast.

The most important mineral in basalt is Mg-olivine. The mineral dissolves in the soils according to the following reaction:

$$4Mg^{2+} + SiO_4^{4-} + 4 H_2O \rightarrow 4Mg^{2+} + Si(OH)_4 + 4OH^2$$

The reaction shows that Mg-olivine releases huge amounts of hydroxyl ions; in fact, the amount released is more than that of GML reaction. It is seen that silicic acid  $[Si(OH)_4]$ is simultaneously released by the reaction, the form of Si that can be taken up by rice (Shamshuddin et al., 2014). Rice growth in a pot without the addition of ground basalt is shown in Figure 17(a). It did not grow at all due to the effects of low pH and/or Al toxicity. At harvest, rice plants almost died probably due to the extreme effects of H<sup>+</sup> and/or Al<sup>3+</sup> stress (Shamshuddin et al., 2014).

Due application of 4 t basalt ha<sup>-1</sup>, showed that rice in the same experiment grew normally, producing yield more than

#### Sustainable Rice Cultivation on Acid Sulfate Soils



*Figure 17.* Rice grown on acid sulfate soil (a) growth affected severely by Al toxicity in the control treatment; (b) rice grown normally in the pot treated with basalt *Source.* Shamshuddin et al. (2011)

4 t ha<sup>-1</sup> (Figure 17(b)). This is commendable considering the low rate of basalt dissolution in the soil even though it was undergoing weathering under acidic condition. If rice is grown again in the same pot, the yield is expected to be higher than that of the first crop as more basalt would have been dissolved.

# Alleviating Al toxicity and/or soil acidity using microorganisms

Soil contains living microorganisms. Some of these microorganisms can be put to good use, such as to improve the productivity of acidic soils. A case in point is the phosphatesolubilising bacteria living naturally in acid sulfate soils. Panhwar et al. (2014b) had isolated and subsequently identified three potential phosphate-solubilising bacteria in acid sulfate soils in the paddy fields of Semerak, Malaysia. The PSB identified were *Burkholderia thailandensis, Burkholderia seminalis* and *Sphingomona spituitosa*. The PSB were found to be able to make P more available from the otherwise insoluble FePO<sub>4</sub> and/or AIPO<sub>4</sub> occurring in acid sulfate soils. This phenomenon would partly solve the problem of P-fertiliser being lost via fixation after it is applied in the paddy fields.

The results of this study showed that the PSB inoculated into rice plants released organic acids under the stress of high Al concentration. Like the case of organic acids secreted by rice roots, Al in the soil will be chelated and consequently inactivated. This is another mechanism by which PSB helps improve the environmental condition for rice growth. To prove that inoculation of rice seedling with PSB improves its growth, a short-term experiment was conducted in the laboratory. The results of the experiment are presented in Figure 18. It is clear that rice seedling inoculated with PSB was bigger/ taller than those without inoculation.

Results also showed the ameliorative effect of PSB. The microbes existing in the rice seedling produced indole-acetic acid, a plant hormone that helps enhance rice growth significantly. This is yet another finding that excites researchers working with the PSB isolated from acid sulfate soils.



*Figure 18.* Comparison of rice seedling with and without bacterial inoculation *Source.* Panhwar et al. (2014b)

Their action in the rice plants had resulted in significant pH increase (Figure 19). For the control treatment, soil pH was about 4, but when the seedling was inoculated with the PSB, soil pH was increased to above 6, regardless of the initial Al concentration. It is believed that during the process expedited by the PSB that takes place in the rice root, exopolysaccharide was released for the increase in soil pH (Panhwar et al., 2014b).

#### Increasing rice yield in Malaysia

The study on the alleviation of soil acidity as well as Al and/or Fe toxicity that affects rice production is not complete without conducting field trials in the areas subjected to the above-mentioned constraints. Hence, in Malaysia, field work was conducted in the Kelantan Plains (Shamshuddin, 2006) and Merbok, Kedah (Azura et al., 2014). Recently, another field trial was conducted in Semerak. The results on the chemical properties of the Semerak trial are presented in Table 1.



*Figure 19.* Effects of PSB inoculation on water pH at various concentrations of Al *Source*. Adapted from Panhwar et al. (2014b)

The topsoil pH of the control treatment was about 4. However, deep down the soil profile, the value was < 3.5, indicative of the presence of pyrite and/or jarosite in the soil. The exchangeable Ca and Mg were insufficient for rice growth, but the exchangeable Al and extractable Fe were very high. The exchangeable Al in the subsoil was  $> 5 \text{ cmol}_c \text{ kg}^{-1}$  soil, above the level known for normal growth of rice plants. On applying the amendments, the fertility of the soil was somewhat improved. This is seen by the increase of exchangeable Ca and Mg with concomitant decrease of exchange Al to a level < 1 cmolc kg<sup>-1</sup>. Although soil pH was still below 5, the condition was believed to be good enough for the rice plants to grow normally because they have the ability to protect themselves against acidity as well as Al and/ or Fe toxicity (Shamshuddin et al., 2013; Shamshuddin et al., 2014; Alia et al., 2015).

The improved soil fertility due to the treatments was reflected by increase in the rice yield (Table 2). T5 in which 6 t GML ha<sup>-1</sup> was applied in combination with JITU

Treatments	pН	Exchang	Exchangeable cations (cmol <sub>c</sub> kg <sup>-1</sup> )					
		Са	Mg	K	Al	Fe (mg kg <sup>-1</sup> )		
Control	3.7c	0.49d	0.61e	0.26c	2.13a	208.45a		
GML (4 t ha-1)	3.9b	1.30c	1.23d	0.30b	1.44b	66.15b		
GML (4 t) + organic fertilizer (0. 25 t) ha <sup>-1</sup>	4.3a	1.60b	1.84b	0.35a	0.93c	31.78d		
GML (6 t ha-1)	4.1b	1.59b	1.54c	0.31b	1.03c	50.55c		
GML (6 t) + organic fertilizer (0.25 t) $ha^{-1}$	4.4a	1.92a	2.07a	0.39a	0.49d	27.49e		

 Table 1

 The chemical properties of the topsoil in Semerak, Kelantan, at rice harvest

\*Organic fertilizer = JITU, GML = ground magnesium limestone

Means within the same column followed by the same letters are not significantly different at P>0.05 (n=5)

 Table 2

 Effects of different treatments on the rice growth cultivated in acid sulfate soil

Treatments	Grain yield (t ha <sup>-1</sup> )	Panicle number (10 <sup>4</sup> ha <sup>-1</sup> )	Spikelet number (panicle <sup>-1</sup> )	Filled spikelet (%)	1000 grain weight (g)
Control	2.12d	553c	77.5c	74.84d	21.78cd
GML (4 t ha <sup>-1</sup> )	3.04c	651b	78.5c	84.71c	22.34c
GML (4 t) + *organic fertilizer (0. 25 t) ha <sup>-1</sup>	3.99b	707a	83.5b	90.12a	26.41b
GML (6 t ha <sup>-1</sup> )	3.62b	701a	100.5a	88.81b	23/17c
GML (6 t) + *organic fertilizer (0.25 t) ha <sup>-1</sup>	4.77a	715a	81.25b	91.69a	31.67a

\*Organic fertiliser = JITU, GML = ground magnesium limestone

Means within the same column followed by the same letters are not significantly different at P>0.05 (n=5)

(an organic fertiliser fortified with effective microorganisms and growth hormones) gave the best yield of about 5 t ha<sup>-1</sup> season<sup>-1</sup>. However, it is not economical to apply lime at this rate.

# Sustainable rice cultivation on acid sulfate soils

An innovative agronomic practice for adoption by farmers is important for rice production to be sustainable. The best approach is to examine all the important findings of past research on rice and subsequently design a special field trial to test the proposed idea. If the results look promising, the proposed agronomic practice should be fine-tuned before it is tested in a large-scale trial using farmer's land.

We have carried out short-term experiments in a glasshouse to test the suitability of GML, ground basalt, biofertiliser as amendments to alleviate the infertility of acid sulfate soils for sustainable rice cultivation. The result clearly showed that bio-fertiliser or bio-fertiliser in combination with GML gave the best yield. However, it is believed that the ameliorative effects of ground basalt were not been fully realised. Basalt takes longer than 6 months to be completely disintegrated and dissolved (Shazana et al., 2013), and it subsequently increases soil pH and releases Ca, Mg, K, P and Si for the uptake by rice. To be sure, if second crop of rice is grown in the same pots, the results might have been completely different. It is highly probable that basalt treatment would give a much better yield. The best yield would definitely come from basalt treatment in combination with biofertiliser.

The results of another experiment using the same amendments are presented in Figure 20. The objective of this experiment was to determine the long-term ameliorative effects of the amendments. It is clear that control treatment gave the lowest grain yield of about 3 t ha<sup>-1</sup> season<sup>-1</sup>. The yield increased significantly after the application of biofertiliser, However, the yield decreased slightly with time, indicating that biofertiliser must be used regularly, perhaps annually.

The ameliorative effects of GML treatment can last for at least three consecutive seasons, with grain yield remaining at about 5 t ha<sup>-1</sup> season<sup>-1</sup>. The best yield in this study was obtained by applying GML in combination with bio-fertiliser (Table 3). The authors believe that basalt in combination with bio-fertiliser (having PSB) actually offers the best option for adoption by farmers in Malaysia or even Southeast Asia. It is clear from Figure 20



*Figure 20.* Long-term effects of GML and basalt with or without bio-fertiliser application on rice growth (a) grain yield; (b) straw yield

that grain yield is steadily increasing. As more ground basalt disintegrates, soil fertility improves further resulting in increased yields. The ameliorative effects of basalt application could last for a long time, perhaps 2 to 3 years. This would translate into lower cost of rice production compared with the conventional practice. Hence, we can grow rice sustainably on acid sulfate soils by applying basalt in combination with bio-fertiliser. In this way, the SSL level in Malaysia can be increased significantly.

Research on the application of biochar for agricultural production is being conducted worldwide with conflicting results. Our rice research group at Universiti Putra Malaysia conducted a field trial in Semerak, Kelantan to test the effects of

Treatments	Number of Panicle plant <sup>-1</sup>	Size of panicle plant <sup>-1</sup>	Number of grains pot <sup>-1</sup> (g)	Weight of grains pot <sup>-1</sup> (g)	Plant biomass (g pot <sup>-1</sup> )
Control	3d	19.33c	515e	8.10e	14.30e
Bio-fertilizer	6a	23.31a	1106a	17.92a	26.53a
GML	5b	22.77b	854b	14.80b	18.98c
Basalt	4c	22.19b	601d	9.09d	16.07d
Bio-fertilizer+GML	5b	23.12a	879b	14.91b	20.45b
Bio-fertilizer+Basalt	4c	20.65c	695c	10.35c	18.34c

Table 3					
Effects of	GML and	basalt with	or without	bio-fertiliser	application

GML = ground magnesium limestone

Means within the same column followed by the same letters are not significantly different at P>0.05 (n=5)

Table 4Effects of GML and biochar with or without bio-fertiliser application

Treatments	Grain yield (ha <sup>-1</sup> )	Straw yield (ha <sup>-1</sup> )	Number of filled grains (%)	Number of panicle plant <sup>-1</sup>	Size of panicle (cm)	Soil pH (After 30 DAS)
Control	3.20e	8.24d	76.61d	11c	20.03d	4.08c
GML	4.04d	8.70c	81.65c	15b	21.61c	5.39b
Biochar	4.54c	9.38b	82.64c	16b	22.00c	5.18b
GML+Bio-fertilizer	5.44a	10.20a	85.89a	18a	24.40a	5.66a
Biochar+ Bio-fertilizer	5.04b	9.98a	83.61b	17a	23.11b	5.40a

\*GML = Ground magnesium limestone 4 t ha<sup>-1</sup>, bio-fertilizer 4 t ha<sup>-1</sup>, biochar 5 t ha<sup>-1</sup>.

Means within the same column followed by the same letters are not significantly different at P>0.05 (n=5)

applying GML and biochar with or without bio-fertiliser. The results of this field trial are shown in Table 4. The best treatment os still GML in combination with bio-fertiliser. The GML and biochar treatment gave reasonable rice yield of about 4 t ha<sup>-1</sup>.

### CONCLUSION

Rice has been planted on acid sulfate soils in Southeast Asia for many years. Due to the stress of low pH and the presence of high Al and/or Fe in the water of the fields, rice yields in the area are often below the national average. High acidity and Al and/or Fe toxicity are the result of pyrite oxidation due to its exposure to the atmospheric conditions when the areas are opened up for agriculture production. The infertility of the soils can be alleviated for sustainable rice production by applying ground magnesium limestone or basalt in combination with bio-fertiliser fortified with phosphate-solubilising bacteria. The bacteria not only excrete organic acids that inactivate Al and/or Fe via chelation, but also increase water pH to above 6. The latter reaction results in the precipitation of Al as inert Al-hydroxides. Rice plants are also able to excrete organic acids via their roots under the stress of high Al and/or Fe that further reduce the availability of both metals in the water. In the end, rice will be able to grow well, giving reasonable yield.

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