Amelioration of actual acid sulfate soils to improve soil chemical properties and rice yields

E Maftu’ah, Y Lestari, E B Pangaribuan and V Mayasari

Indonesian Swampland Agricultural Research Institute, Banjarbaru, Indonesia
E-mail: eni_balittra@yahoo.com

Abstract. This study aim was to determine the effectiveness of various types of ameliorant in improving soil chemical properties and rice yields in actual acid sulfate soils. The study was conducted in Tamban Baru Tengah village, Tamban Catur Subdistrict, Kapuas, Central Kalimantan, from April-September 2019. The research design used a Randomized Block Design with treatment (A1) 5 t ha⁻¹ of lime given once at the beginning, (A2) 3 t ha⁻¹ lime + 2 t ha⁻¹ lime given at the rice age of 1 month, (A3) 3 t ha⁻¹ lime + 2 t ha⁻¹ 'Porre' organic fertilizer, (A4) 3 t ha⁻¹ lime + 2 t ha⁻¹ rice husk ash. Each treatment was replicated 4 times. Periodic soil observations included pH H₂O, EC, SO₄²⁻, Fe²⁺ and Al³⁺, plant height, tillers number, and rice yields were observed. The results showed that the ameliorant treatment was able to reduce concentration of Fe²⁺ at planting from 6400 ppm to 1000-1500 ppm, SO₄²⁻ from 8000 ppm to 2100 to 4300 ppm, Al³⁺ from 16.31 cmol(+)/kg⁻¹ to 5.2-6.7 cmol(+)/kg⁻¹. Lime combined with “Porre” organic fertilizer (A3) gave the highest rice yield (>17% higher than A1). The use of “Porre” organic fertilizer was able to reduce the use of lime in tidal swampland.

1. Introduction
Inappropriate reclamation of acid sulfate soils can change the sulfidic material from reductive to oxidative. Andersen et al. [1] stated that if pyrite is oxidized, a number of H⁺ ions are produced which causes acid sulfate soil to become very acidic. Actual acid sulfate soils are acid sulfate soils that have a sulfuric or pyrite horizon that has been oxidized at a depth of 0–50 cm. The topsoil of actual acid sulfate soils has a field pH <3.5 and sulfuric horizon or signs of a sulfuric horizon due to oxidation of pyrite as a result of excessive drainage. If the pH of the field reaches <3.5, it can result in the clay lattice being destroyed, so that Al³⁺ ions are very dominant in the sorption complex [2].

The actual acid sulfate soil requires special handling to increase the productivity of the land. Land management is one of the most important factors in achieving optimal and sustainable results. Therefore, land management must be attempted without causing any damage to the environment or reducing the quality of land resources, and should be directed at improving the physical, chemical and biological of soil properties.

High soil acidity can increase the solubility of iron (Fe), aluminum (Al), and manganese (Mn) to a level of toxicity to plants, cause deficiency of phosphorus (P). High Al and Fe concentrations in acid sulfate soils can be toxic for plants. The root was part of the plant that most sensitive to Al toxicity [3]. Fe
toxicity causes physiological changes in rice plants so inhibit plant growth [4]. Improvement of soil properties through amelioration is needed to support the success of utilizing the actual acid sulfate land. However, if the presence of pyrite in the top soils is high, it will limit the use of swamp land for agriculture because it is a source of acidification, which requires a lot of ameliorant so that it is no longer economical. Theoretically, 1% pyrite content in the root zone results in soil acidity of more than 30 meq, which means that the materials (e.g. lime) needed for neutralizing is more than 40 t ha$^{-1}$ [5]. In general, lime between 0.5 and 3.0 t ha$^{-1}$ is sufficient [6]. Therefore, to increase the effectiveness of amelioration in actual acid sulfate soils, it is necessary to add other ameliorant materials besides agricultural lime. The ameliorant material can be in the form of dolomite lime or organic matter [7], organic fertilizers, mineral soils, zeolites, dolomite, natural phosphates, manure, agricultural lime, husk ash, purun tikus (Eleocharis dulcis) [8], lime, mineral soil, manure, compost and ash [9]. Amelioration research is mostly carried out in potential acid sulfate land, while for actual acid sulfate land there is little information about ameliorant which is effective in improving soil properties and rice production. The production of rice in actual acid sulfate land is generally less than 3 t ha$^{-1}$ with a cropping index of one time a year [10]. This study aim was to determine the effectiveness of various types of ameliorant in improving soil chemical properties and rice yields in actual acid sulfate soils.

2. Materials and methods

2.1. Materials

Materials used in this research, among others; rice husk biochar, rice husk ash, ‘Porre’ organic fertilizer, agricultural lime, manure, biological fertilizer (Biotara), paddy seed, Urea and NPK fertilizers, herbicides, fungicides, insecticides and chemicals for soil and water analysis.

2.2. Methods

The study was conducted in Tamban Baru Tengah village, Tamban Catur Subdistrict, Kapuas, Central Kalimantan, from April to September 2019. The research design used a Randomized Block Design with treatments: (A1) 5 t ha$^{-1}$ lime given once at the beginning, (A2) 3 t ha$^{-1}$ lime given at beginning + 2 t ha$^{-1}$ lime given at the rice age of 1 month, (A3) 3 t ha$^{-1}$ lime + 2 t ha$^{-1}$ ‘Porre’ organic fertilizer given at beginning, (A4) 3 t ha$^{-1}$ lime + 2 t ha$^{-1}$ rice husk ash given at beginning. Each treatment was replicated 4 times and all treatments were given manure at a dose of 2 t ha$^{-1}$.

Land clearing is carried out using herbicides and mechanization. The land is cleared from various types of weeds by means of minimum tillage using a hand tractor with a depth of 30 to 35 cm. After land clearing, the layout is carried out according to the treatment. The plot size was 17 m x 17 m, and total plots number were 12, in accordance to the number of treatments and replications. The ameliorant application is carried out after the land is processed and ready for planting, that before ameliorant application soil samples were taken from each plot for initial soil analysis. Rice seedlings of Margasari variety were planted 2 weeks after ameliorant application. Planting was done using 4:1 ‘Legowo’ row system. Rice seedlings were planted at a spacing distance of 20 cm x 22.5 cm.

The basic fertilizers given were N, P, K originating from urea and NPK Pelangi. The recommended dosage is 300 kg ha$^{-1}$ NPK (15:15:15) and 100 kg ha$^{-1}$ prilled urea. The urea fertilizer was applied splitly in stages three times, namely a third part at seven days after planting (DAP) together with the entire dose of NPK fertilizer.

Retransplanting of dead plants or poor plant growth was done at the age of 7 days after planting using spare seeds. Pest and disease attacks were controlled according to the intensity of their attack by using recommended vegetable pesticides or insecticides or fungicides. Weeding was done at the age of 30 and 60 days after planting using a power seeder or manually by removing the growing weeds.
The parameters observed included the growth and yield of rice. Observation variables included soil properties, plant growth, and rice yield. Periodic soil analysis included pH, EC, Fe, and SO$_4^{2-}$ at 0, 30, 45, and 90 days after planting (DAP). Plant parameters observed included plant height and number of tillers. While observation on production included the number of filled and empty grains per panicle, weight of 100 grains, yield per plot, yield per ha. Data were analyzed using F test, followed by the least significant difference test (LSD) at α 5%.

3. Results and discussion

3.1. Actual acid sulfate soil characteristics

The results of soil analysis on the top layer (0-50cm) showed very acid (H$_2$O pH 3.52) soil reaction, very high exchangeable concentration of Al 16.51 cmol(+)/kg, SO$_4^{2-}$ (8235 ppm), and pyrite (around 5.2%) (table 1).

| Soil properties                          | value   | Criteria   |
|-----------------------------------------|---------|------------|
| 1. pH-H$_2$O                            | 3.52    | Very acid  |
| 2. pH-KCl                                | 3.36    | Very acid  |
| 3. Electric conductivity (mS/cm)         | 0.461   | Low        |
| 4. Exchangeable Al (cmol(+)/kg)          | 16.51   | Very high  |
| 5. Exchangeable H (cmol(+)/kg)           | 4.61    | Very high  |
| 6. FeS$_2$ (%)                           | 5.212   | Very high  |
| 7. Available Fe$^{2+}$ (ppm)             | 6387.94 | Very high  |
| 8. Available SO$_4$(ppm)                 | 8235.98 | Very high  |

Enio et al. [11] stated that if the pyrite contained in the sulfidic material is oxidized, a number of H$^+$ ions are produced which causes the acid sulfate soil to become very acidic. High soil acidity can increase the solubility of iron (Fe), aluminium (Al), and manganese (Mn) in the level of toxicity to plants, and deficiency of phosphorus (P) because it is strongly bound by Fe and Al, and low base cations due to leaching loss. Increasing exchangeable Fe, Al and Mn can decrease P-available.

The high concentration of H$^+$ ions in the soil solution can cause soil acidity, this illustrates that the oxidation process that occurs in the soil is very strong. Sudarmo [12] stated that acidity due to the oxidation of acid sulfate soil causes aluminosilicate minerals to dissolve, characterized by the increased Si-Al concentration in the soil solution suspension. Oxygen and Fe$^{3+}$ ions in the soil can act as oxidizing agents for pyrite which causes the soil to become very acidic [13] and the soil pH value is very low, reaching 2 to 3. The H$^+$, Fe$^{2+}$, and SO$_4^{2-}$ ions produced due to low pH values can also increase free Fe [14].

Very acidic soil conditions, high concentrations of Fe, Al, and sulfate are very detrimental for rice plants. Al toxicity can reduce and damage root systems, causing plants to be susceptible to drought stress and nutrient deficiency [15]. Ryan and Delhaize [16] stated that Al can damage the roots while they are still in the cell wall without having to enter the cell. Symptoms of chlorosis in leaves began to appear at a concentration of 240 ppm Al in nutrient solution [17].

Increasing the concentration of Fe in nutrient solution can cause a decrease in plant biomass. The higher the Fe concentration in the nutrient solution causes the growth of rice plants to become increasingly depressed. As stated by Fageria et al. [4], rice plants that experience iron toxicity will inhibit plant growth.
3.2. Effect of amelioration on soil chemical properties

Amelioration treatment affects periodically on soil chemical properties, namely pH, EC, Fe$^{2+}$, SO$_4^{2-}$ and Al$^{3+}$. Although ameliorant treatment has an effect on the observed soil chemical properties, the dynamics of soil chemical properties are more influenced by soil oxidation and reduction conditions. The treatment that gave the highest pH increase at planting time was A3 treatment, namely “Porre” organic fertilizer 2 t ha$^{-1}$ + lime 3 t ha$^{-1}$, and the lowest was treatment A2, namely lime 3 t ha$^{-1}$ before planting + 2 t ha$^{-1}$ at the plant age of 1 month. However, at harvest time the lowest pH was shown by treatment A1 and the highest was in treatment A2 which was not different from A3 (figure 1a). Apart from the treatment effect, pH fluctuation is also caused by soil oxidation and reduction conditions. “Porre” organic fertilizer is formulated with biochar raw materials from rice husks and manure to improve the chemical properties of actual acid sulfate soils. Biochar can increase soil fertility through increasing soil pH [18], increasing nutrient availability [19], nutrient retention [20], and cation exchange capacity [21]. Lehmann et al. [20] explained that biochar was able to increase fertilization efficiency.

The value of the electrical conductivity (EC) of the soil due to ameliorant treatment is shown in figure 1b. In the initial period, the EC was relatively similar, but after 30 weeks until harvest time, the treatment of 2 t ha$^{-1}$ of rice husk ash + 3 t ha$^{-1}$ of lime (A4) gave the lowest EC value compared to other treatments. Rice husk ash treatment is not strong enough compared to rice husk biochar to retain ions in the soil. EC is more affected by the wetting (dilution) and drying conditions. The effects of wetting and dilution appear to greatly reduce EC in acid sulfate soils [22]. During planting, where the ameliorant application has occurred, there is a decrease in EC levels, which is thought to be due to reduced levels of ions such as SO$_4^{2-}$ and Al$^{3+}$. Then there was an increase in the value of soil EC for all treatments given. This condition is caused by drying so that the ionic concentration in the soil solution increases. The lowest EC value is shown by treatment A4 (figure 1b).

![Figure 1](image-url)

**Figure 1.** Changes in soil pH-H$_2$O (a) and soil EC (b) due to ameliorant treatment. Note: A1 = Lime 5 t ha$^{-1}$ (before planting), A2 = Lime 3 t ha$^{-1}$ (before planting) + 2 t ha$^{-1}$ (1 month age), A3 = Lime 3 t ha$^{-1}$ + ‘Porre organic fertilizer” 2 t ha$^{-1}$ (before planting), A4 = Rice ash husk 2 t ha$^{-1}$ + 3 t ha$^{-1}$ lime (before planting).

Provision of ameliorant can reduce the concentration of Fe$^{2+}$ and SO$_4^{2-}$ from 6400 ppm for Fe$^{2+}$ and 8200-8300 for SO$_4^{2-}$ to around 2100 to 4300 ppm at planting time (figure 2). In the initial period the lowest Fe concentration was shown by treatment A2, but at the end of the observation the lowest Fe
concentration was in treatment A3. Fe concentration fluctuations occurred at each observation period. This condition is related to soil oxidation and reduction conditions. Oxidation and reduction conditions can be seen from the groundwater level in the canal, where in the research location there is a relationship between the water level in the channel and in the land.

The concentration of ferrous iron ($\text{Fe}^{2+}$) is lower than sulfate ($\text{SO}_4^{2-}$) reaching 4300 ppm at planting time, while $\text{Fe}^{2+}$ only ranges from 1500 to 2500 ppm. Reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ can occur at around Eh $+360\text{mV}$ [23], so even though the soil is dry (not inundated), $\text{Fe}^{2+}$ is still found (figure 2a). The pattern of $\text{Fe}^{2+}$ concentration tends to be closer to redox conditions [24]. $\text{Fe}^{2+}$ concentration increases with increasing groundwater level and reductive conditions. In flooded conditions ferrous iron in acid sulfate soils often creates problems [25]. The range of $\text{Fe}^{2+}$ levels in inundated acid sulfate soils is quite wide, 0.07 to 6600 ppm, which depends on pH, organic matter, levels and reactivity of $\text{Fe}^{3+}$ [26].

According to Moses and Hermann [27] soil acidity occur in acid sulfate land is as follows:

\[
\begin{align*}
\text{FeS}_2(s) + 7/2 \text{O}_2 + \text{H}_2\text{O}(l) & \rightarrow \text{Fe}^{2+}(aq) + 2\text{H}^+(aq) + 2\text{SO}_4^{2-} \quad (1) \\
\text{Fe}^{3+}(aq) + 1/4\text{O}_2(aq) + \text{H}^+(aq) & \rightarrow \text{Fe}^3+(aq) + 1/2\text{H}_2\text{O}(l) \quad (2) \\
\text{FeS}_2(s) + \text{Fe}^{2+}(aq) + 8\text{H}_2\text{O}(l) & \rightarrow 2\text{Fe}^{3+}(aq) + 16\text{H}^+(aq) + 2\text{SO}_4^{2-} \quad (3) \\
\text{Fe}^{2+}(aq) + 1/4\text{O}_2(aq) + 3/2\text{H}_2\text{O}(l) & \rightarrow \text{FeO}.\text{OH}(aq) + 2\text{H}^+(aq) \quad (4)
\end{align*}
\]

The oxidation of pyrite in 1st equation is slow, the oxidation of pyrite with the oxidant $\text{Fe}^{2+}$ (3rd equation) is faster than in 2nd equation. The concentration of $\text{Al}^{3+}$ in the study location was very high. At the initial time, the Al concentration reached 16.31 cmol(+)/kg(-1). The 5 t ha(-1) amelioration treatment was able to reduce the $\text{Al}^{3+}$ concentration at 2 weeks after application to about 5.2 to 6.7 cmol(+)/kg(-1). At the end of the observation, there was an increase in $\text{Al}^{3+}$ concentration for all treatments, even in the 3 t ha(-1) lime treatment which was given once at the beginning (A1), the Al concentration returned to its initial condition. Whereas in the lime treatment which is divided by 2 times (A2), the increase in Al is not as
drastic as if the lime is given once at the beginning (A1). The application of ameliorant "Porre" (A3) was able to reduce the Al concentration higher at the end of the observation than other treatments (figure 3).

![Figure 3. Al³⁺ changes due to ameliorants treatment. Note: A1 = Lime 5 t ha⁻¹ (before planting), A2 = Lime 3 t ha⁻¹ (before planting) + 2 t ha⁻¹ (1 month age), A3 = Lime 3 t ha⁻¹ + “Porre organic fertilizer” 2 t ha⁻¹ (before planting), A4 = Rice ash husk 2 t ha⁻¹ + 3 t ha⁻¹ lime (before planting).](image)

3.3. Effect of amelioration on growth and yield of rice

The amelioration treatments affect rice plant growth as presented in table 2. Ameliorant types did not have a significant effect on the tillers number, but significant on plant height at 7 weeks after planting (WAP).

| Treatment | Number of tillers | Plant height (cm) |
|-----------|------------------|------------------|
|           | 3 WAP | 5 WAP | 7 WAP | 3 WAP | 5 WAP | 7 WAP |
| A1        | 19.87 | 28.00 | 24.93 | 69.33 | 84.67 | 114.53 b |
| A2        | 19.07 | 26.50 | 27.47 | 74.07 | 91.98 | 128.27 a |
| A3        | 18.07 | 33.00 | 23.87 | 77.40 | 92.60 | 122.27 ab |
| A4        | 19.13 | 32.00 | 23.80 | 79.87 | 94.80 | 125.27 a |

Note: A1 = Lime 5 t ha⁻¹ (before planting), A2 = Lime 3 t ha⁻¹ (before planting) + 2 t ha⁻¹ (1 month age), A3 = Lime 3 t ha⁻¹ + “Porre organic fertilizer” 2 t ha⁻¹ (before planting), A4 = Rice ash husk 2 t ha⁻¹ + 3 t ha⁻¹ lime (before planting), WAP = week after planting; numbers followed by the same letter, not significantly different based on LSD test at α 5%.

The treatment that showed the best growth was A2 treatment 3 t ha⁻¹ at the beginning of + 2 t ha⁻¹ at the age of the plant for 1 month, but it was not significantly different from all treatments except A1. Treatment of lime as much as 5 t ha⁻¹ (A1) which is given once at the beginning is less effective when compared to giving in split (divided), even the plant height in treatment A1 is lower than that in A2, A3 and A4. Amelioration treatment affects the yield components of rice. The highest number of panicles was
indicated by the A3 treatment, the largest panicle weight and also the largest number of empty grains on A4 (table 3).

| Treatment | Number of panicles per plant | Weight of panicles (g) | Number of filled grains per plant | Number of empty grain per plant |
|-----------|------------------------------|------------------------|----------------------------------|-------------------------------|
| A1        | 25.29 b                      | 22.33 b                | 50.08 ns                         | 21.64 b                       |
| A2        | 25.66 b                      | 21.37 b                | 48.98 ns                         | 24.10 ab                      |
| A3        | 30.38 a                      | 24.39 b                | 50.74 ns                         | 22.41 b                       |
| A4        | 25.50 b                      | 24.36 a                | 50.19 ns                         | 29.03 a                       |

Note: A1 = Lime 5 t ha⁻¹ (before planting), A2 = Lime 3 t ha⁻¹ (before planting) + 2 t ha⁻¹ (1 month age), A3 = Lime 3 t ha⁻¹ + “Porre organic fertilizer” 2 t ha⁻¹ (before planting), A4 = Rice ash husk 2 t ha⁻¹ + 3 t ha⁻¹ lime (before planting), WAP = week after planting; numbers followed by the same letter, not significantly different based on LSD test at α 5%; ns=not significantly.

The effectiveness of agricultural lime on actual acid sulfate soils was higher in the application time method that split twice, namely at 1/2 dose at planting time, and 1/2 dose at the age of 1 month plants (A2), compared to the one-time application at the time of planting (A1). The treatment of A3 gave the highest rice yields reaching 2.64 t ha⁻¹ and was not significantly different from A2 and A4. These results were higher when compared to rice yields. Margasari variety in Karang Dukuh village amounted to 2.51 t ha⁻¹ [28].

The application of “Porre” organic fertilizer can increase rice yields by about 17% compared to lime application, and reduce the use of lime by the dose of organic fertilizer given. The Porre organic fertilizer is an organic fertilizer formulated from livestock waste and harvest waste (rice husk) which has been processed into biochar. This formulation has been tested to increase swamp soil fertility and at the same time reduce GHG emissions in swamps. The content of organic “Porre” fertilizers is pH ranging from 7.3 to 7.8, organic C around 20%, N-total 0.9 - 1.1%, CaO 2.30 to 2.50% and MgO 0.50 to 0.60 % [29].
4. Conclusions
Amelioration affects the chemical properties of the actual acid sulfate soils. The higher effectiveness of agricultural lime occurred at application two stages i.e. at beginning and 1 month after planting than that given at the beginning. Application of 3 t ha\(^{-1}\) agricultural lime combined with 2 t ha\(^{-1}\) organic fertilizer by “Porre” can suppress Fe\(^{2+}\), sulfate and Al\(^{3+}\) concentrations up to >40%, 50% and 45% respectively and increased rice yields up to >17% compared to 5 t ha\(^{-1}\) lime. “Porre” organic fertilizer can reduce the use of lime in agricultural land.

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