Mitigation of pyrite oxidation impact in tidal swamp management for agriculture

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Abstract. Reclamation of tidal swamps will increase the opportunities of pyrite oxidation which causes severe acidification. Pyrite oxidation occurs due to over drained and pyrite exposed to oxygen. The acidification process is unavoidable; therefore, mitigation efforts needed to minimize adverse impacts. In general, mitigation efforts can be done with 2 approaches, namely preventive approach, an effort to prevent continued acidification, and curative approaches, an effort to rehabilitate degraded land. Land use planning with detailed engineering design is the first step to mitigate the effects of pyrite oxidation. Mitigation efforts for acidified soil can be using water management techniques to leach toxic elements out from the root zone. Many research results revealed that one-way flow system water management was effective to reduce toxic element. High soil acidity and toxic element can also reduce by applying soil ameliorant such as 0.5 to 2.0 t ha\(^{-1}\) of lime. It’s can increase soil \(pH\), plant growth and fertilizer use efficiency. Strong acid soils also cause low nutrient status due to intensive leaching and fixation. Therefore, nutrient supply trough fertilization is needed. Finally, mitigation efforts can also be done by planting acid tolerant rice varieties that resulted from long time rice research in tidal swamps. This paper described some efforts should be done to mitigate pyrite oxidation impacts for agriculture.

1. Introduction

Tidal swamp land is part of a swampy ecosystem which is relatively close to the coast so that its hydrological conditions are influenced by sea tide movement. Base on land resource map, tidal land in Indonesia covers about 9 million ha, spreading mainly on large islands, namely in Sumatra, Kalimantan, Sulawesi, and Papua [1]. This land is potential to be developed into agricultural land because of its flat topography and sufficient water availability. However, despite its advantages, agriculture development on tidal swampland faces several constraints related to the dynamics of the physical and chemical land properties.

Tidal land is belonging to alluvial soil that is formed from fluvio-marine deposits. Specific nature of this land is the presence of pyrite within sub soil layer, so that commonly this land called acid sulphate soil [2]. Pyrite is iron sulphides compound (FeS\(_2\)) which is formed in extremely reductive conditions, where mineral soils containing iron (Fe) are deposited in saline or brackish water environment that rich in sulphate (SO\(_4\)). This strong reductive condition is only possible in the presence of organic matter, so that pyrite is formed in organic matter-rich sediments in the subsoil layer. Pyrite compound or sulfidic layer in tidal swamp land is the main source of problems because when oxidized it will produce sulfuric acid which is causes soil environment to become very acid. In general, the pyrite oxidation process can
occur naturally due to long drought or due to anthropogenic influences such as land reclamation activities.

Pyrite is the most plenty sulphide mineral on the earth and frequently associated with another valuable sulphide minerals such as sphalerite (ZnS), chalcopyrite (CuFeS2), and galena (PbS) [3]. Commonly, pyrite mineral found on coastal plain, however, pyrite is also as an undesired inorganic constituent present in coal mining. Acid mine come from coal mining is associated with its present in coal. Pyrite contains 46.55% Fe, and 53.45% S (by weight) [4].

Subsoil layers containing pyrite has grey color matrix or darker color than its above soil layer (hue 10YR, 2.5Y, 5Y, N, and 5GY; chroma 1) and its depth varies from one place to another places. The occurrence of pyrite is often mixed with the remains of leaves or roots of mangrove or palm trees, and sometimes foul smelling (H2S) [5]. In general, the pyrite content in acid sulphate soils is relatively low, a maximum of 6 to 7% by weight, and the most common content varies from 1 to 4% [6].

Oxidation of pyrite has become a big problem in term of bad impact to soil chemical characteristics in site and the surrounding environment. The oxidation of pyrite causes the soil environment to be very acidic and unsuitable for agricultural development without efforts to improve soil conditions. Leaching of any pollutant from acid sulphate soil involves transferring of toxicities from the root zone to the surroundings and causes the contamination of surface water and creates substantial negative effects on the crops and fish growth in surrounding areas [7, 8]. This paper will describe the process of pyrite oxidation and its impact to soil condition and mitigation measures needed to reduce the adverse effects of pyrite oxidation.

2. Pyrite oxidation and related agronomic impacts

Reclamation of tidal swamp has high impact on soil conditions due to pyrite compound oxidation and developed into acid sulphate soil, except if the land is remained in waterlogged condition. Pyrite compounds within the subsoil layer are only stable under reductive environment or anaerobic condition. When the environmental conditions change to aerobic conditions, pyrite will undergo oxidation to produce dissolved iron and sulfuric acid which are extremely acid. Aerobic conditions allow when groundwater down below the soil layer containing pyrite as a result of deep drainage or it exposed to the soil surface during canal excavation.

Pyrite oxidation by oxygen is a slow process, but it is accelerated by the presence of the autotrophic bacteria *Thiobacillus ferrooxidans* that oxidizing iron II become iron III in solution [5, 9]. Iron III is very soluble at pH <4 and promote catalytic oxidation of pyrite.

The whole reaction is described as follows:

\[
\text{FeS}_2 + \frac{15}{2}\text{O}_2 + \frac{7}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ 
\]

In these reactions, each mole of pyrite releases 4 mole of acidity, so that soil pH drops drastically. However, if the soil has high enough neutralizing compounds, such as OH- ions, lime (CaCO3), exchangeable bases, and weatherable silicate minerals, the soil pH does not decrease lower than pH 4.0. The presence of marine clay which contains enough smectite clay minerals and saturated with bases, is also buffering soil pH. If pH solution > 4, iron III oxides and hydroxides precipitate become rust flux or nodule, which is reddish-brown in colour, on the soil surface and canal walls. Conversely, if pH of oxidizing system < 4, iron III become very soluble and bring rapid oxidation of pyrite [10]. Oxidation process of pyrite by iron III maybe represented by reaction as follows:

\[
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16 \text{H}^+ 
\]

Acidification of acid sulphate soil causes several impacts to other soil properties such as Al and iron toxicity, nutrients lost through leaching, and P fixation by Al and Fe oxides. Exchangeable aluminium (Exch-Al) comes from the breakdown of clay mineral structure due to high soil acidity. Meanwhile dissolved iron released from pyrite oxidation. The high concentration of iron-III, H+ and the presence of
abundant of exch-Al will compete with bases cation so that Ca, Mg and K experienced leaching and cause low in base saturation. Exch-Al and iron in the soil solution will also bind phosphate ions tightly, so that it is not available for plant. As a result, productivity of acid sulphate soil become extremely low.

In high soil acidity, Al toxicity is likely to be the principal hazard for plant growth [5]. Solubility of Al inversely related to soil pH, sharply increase until 10 times for each unit pH decrease. In Thailand case, Al concentration of groundwater about 0.4 ppm at pH 5.5 increased become 54 ppm at pH 2.8 [6]. Al toxicity is occurred in concentration as low as 1 to 2 ppm and varied among crop varieties. High concentration of Al will affect to root growth and inhibiting enzymes concerned with synthesis of cell wall material as result of deformed root system and stunted crop growth [11]. Meanwhile Al saturation of acid sulphate soil in South Kalimantan ranges from 67 to 71% (high to very high) [12].

Iron solubility as a result of pyrite oxidation will be toxic for rice at concentration excess of 9 mol m$^{-3}$ [8]. The resistance of rice plant to iron toxicity varies according to rice varieties. Rice plant which is experienced iron toxicity indicated by brown rusty spot on leaf blade and it is significantly reduced yield of rice. Hydrogen sulphide (H$_2$S) often becomes problem in waterlogged lowland rice and causes akiochi disease which inhibits rice plant roots to absorb nutrients. This is because low pH is unfavourable for organic matter decomposition shown by the C/N ratio varies from high to very high [12], as a result N availability becomes low. Phosphorus deficiency commonly occurred in soil with high soluble Al and Fe. The available P of acid sulphate soil at South Kalimantan is about 12.6 to 19.3 ppm [12]. Meanwhile the exchangeable bases such as Ca, Mg and K become extremely low due to intensive leaching [5]. However, with strong influence of sea water, the value of exchangeable Mg is bigger than Ca. In many places of coastal plain at Kalimantan and Sumatra islands where ASS are abundant, the potential environmental threats have fairly serious impact to the fish habitat [13].

3. Mitigation measures for agriculture development

3.1 Site characterization

Tidal swamp land reclamation for agriculture development must be carefully planned, preceded by land characterization and detailed engineering design (DED). Land characterization and mapping of potential constraints are important because tidal land is not all suitable to be developed for agriculture. Site characterization will determine whether tidal land could be developed or not and to recognized which part of land is safe to be developed for agriculture. If it could be developed, then we should determine the design of the drainage network, and water management technique that will be applied. It will also need to describe or whether soil amendment is required.

In Indonesia, among 9 million ha of tidal swamp land, only 6 million ha were suitable for agriculture [1]. There are many potential constraints that might be as limiting factors. Therefore, detailed planning with concerns to infrastructure development should consider to the site characteristics to avoid adverse impact in the reclamation processes. As previously described, most of tidal swamp land that developed from marine deposits contain an iron sulphides compound, in Soil Taxonomy called as sulfidic material. Sulfidic material which have been oxidized are considered to have undergone a ripening process and changed into sulfuric horizon, known as actual acid sulphate soil. The sulfuric horizon at least has 15 cm thick, pH < 3.5 and composed of mineral or organic soil material located just above the sulfidic material. In Soil Taxonomy, soil great group that belong to acid sulphate soil are Sulfaquents, Sulfaquents, Sulfihemists and Sulfohemists [14].

Tidal swamp is classified into four classes based on its hydrology characteristics namely type A, B, C and D [15]. Type A is tidal land located between mean low tide and mean neap tide, so that it will be experience daily flooding. Type B is tidal land that lies between mean neap tide and mean spring tide, it just experience flooding during spring tide. Type C is land surface above mean spring tide, there is no tidal flooding, but ground water surface lies between 0 to 50 cm below land surface. Type D is tidal land that has ground water surface $>50$ cm. Hydrology classification is important to determine water management practice that will be applied. Tidal irrigation is only an option in type A and B, meanwhile type C and D are permanently drained [16]. However, tidal irrigation can be applied in type C if this land developed surjan system. In short, site characterization and detail engineering design in utilization
of acid sulphate soil for agriculture development is essential to minimize of disturbance and it is considered as preventive measure to avoid land degradation [2].

3.2. Water management

Tidal land reclamation is preceded by the construction of drainage canals to control water according to crop needs. Those canals consist of primary, secondary, tertiary, and quarter canals. The construction of these canals is intended to facilitate water management in tidal areas. Water management consists of irrigation, drainage, flooding or control of groundwater table depth and flushing. Irrigation is an effort to meet crops water requirement by utilizing high tide. Meanwhile, drainage is measured to reduce excess water in the crops root zone. The most important water management on tidal land is intended to leach out acidity and toxic elements by alternating flooding and flushing.

Water management technique for paddy cultivation on tertiary canal level can be done in two approaches depending on the hydrological and hydro-topographic conditions namely one-way flow system and canal blocking system. One-way flow system water management is applied to land types A and B. While the canal blocking system is suitable for land types C and D. Research result presented at Figure 1 showed that one-way flow system can reduce dissolved iron concentrations and reduce exchangeable Al during crops season [17]. For land with higher hydro-topography, the application of the canal blocking system can improve land productivity. Periodic alternate flooding and flushing is required to remove dissolved toxic elements [18]. The pH value of groundwater increased from an average of 4.2 at the time of soil tillage to an average of 4.8 at just after planting and 5.4 at harvest time [19]. While the dissolve Fe$^{2+}$ concentration is 160 ppm at just after planting and 72 ppm at harvest time. The increase in land quality was followed by an increase in the productivity of the Cisadane rice variety up to 6.26 t ha$^{-1}$ and the Cisangarung variety 9.44 t ha$^{-1}$ of dry harvest grain.

To accelerate leaching of toxic elements, Subagyo et al. [18] suggested to build intensive shallow ditch with 6 m distance within the plot and around ditch at the edge of plot. This technique can increase leaching of toxic elements such as Fe$^{2+}$, sulphate, and Al$^{3+}$ and improved soil pH. Simulation Model for Acid Sulphate Soils (SMASS) can predict that in the current conditions of water management by farmers, in the next 5 years, pyrite at a depth of 40 cm will decrease from the initial condition of about 3.9% to around 2.3%, or there is a decrease in pyrite content at an average of about 0.32% per year [20]. With the improvement of water management from the research results, it is predicted that there will be a decrease in pyrite content from about 3.9% to 2%, or an average of about 0.38% per year. This indicate that, presence of pyrite could be eliminated by time through proper water management. However, it should be noted that generally the thickness of the pyrite layer can reach more than 1 meter depending on the location.

![Figure 1. Effect of one-way flow system water management to soluble Fe and exchangeable Al during crops season on acid sulphate soil at South Kalimantan [17].](image)
Continuous re-flooding can increase soil pH and reduced the pyrite oxidation rate. Re-flooding relies on establishing conditions where the reduction of the Fe, Mn, S and N can take place. The reduction of these elements is responsible for the increase in pH that is commonly observed in acid soils after flooding. Re-flooding can also be used as a water table height-management tool to prevent the oxidation of pyrite or further oxidation of ASS [20]. Changes level of the water pH on acid sulphate soils is determined by the level of soil redox (Eh). Flooding of acid sulphate soils has been reported in many studies to cause a decrease in soil Eh conditions, that would increase in soil pH. Conversely, decrease in groundwater levels due to drought or dry season causing an increase in soil Eh.

3.3. Amelioration

Acid sulphate soil (ASS) has many constraints in term of soil chemical properties therefore it is unsuitable for most food crops. Therefore, an effort to reduce adverse impact of those constraints is needed, so that plant growth and productivity can be increased. The application of soil ameliorant such as lime and organic matter could be an option to improve AAS condition. Liming is considered as the most effective and common practice to reduce acidity and Fe toxicity and neutralize excess exchangeable Al on ASS [2, 21 – 23]. Amelioration is conducted by physical incorporation ameliorant with the topsoil prior planting. Lime has an alkaline pH and buffers any acid produced therefore it could increase soil pH. To increase soil pH from 4.1 to 5.6 at ASS, South Sumatera needs 2 t ha⁻¹ lime and it could increase rice yield from 3.18 t ha⁻¹ to 6.4 t ha⁻¹ [24]. If ASS is leached during early stage of acidification or proper water management applied, lime requirement should be lower. Site specific lime and fertilizer requirement can be determine using rapid test kit known as Swampland Soil Test Kit: Acid Sulfate Soils or PUTR in Indonesian. Apart from those constraint, farmers faced many technical problems on their cultivation in AAS [25]. Incorporation of organic matter on acid soil could improve the soil condition and nutrients availability due to increase soil pH and decrease exch-Al [26, 27, 21]. Mixing of ASS with an alkaline material such as lime was observed to prevent either a sulphides material soil from acidifying or neutralized the residual effects of a sulphuric soil [4]. The current knowledge on understanding the impacts of plants growing on ASS under different moisture regimes are limited to very few studies [28] and warrants further research [13]. Previous study in Malaysia showed that Al³⁺ toxicity in ASS was reduced when peat, or peat in combination with manure, rice straw, and palm oil mill sludge were added [29].

3.4. Fertilization

High soil acidity makes several soil nutrients less available to plants. The acid dissolves iron and Al from the soil and fix P become less available to plants. It is reported that there had been deficiency of macro (K, Ca, Mg) and micro (Mn, Zn, Cu, and Mo) nutrients in various acid sulfate soils in the tropics [30]. The excess of Al dan H in soil solution will compete and dominate clay mineral exchange complex and liberate Ca, Mg and K so that underwent leaching. Nutrient status, especially macro nutrient, of ASS are typically low. Therefore, fertilization has become important to meet crops nutrients requirement. Rice plants are very responsive to N and P fertilization on acid sulphate soils. P requirement for rice at ASS South Kalimantan is about 100 to 135 kg P₂O₅ ha⁻¹ [31, 32]. Usage of phosphate rock (PR) as source of P is more effective compare to TSP or SP-36 since PR has neutralizing effect to soil acidity [33]. K requirement for rice in ASS is about 75 to 100 kg K ha⁻¹ at Sumatera and Kalimantan.

3.5. Growing tolerant crops

Adaptability of crops to ASS varies according to species or variety. Among food crops, rice is the most preferable crop which is highly acid tolerant. Flooding condition during planting season will prevent pyrite from oxidation. There are many tolerant high yielding rice varieties have been introduced such as Inpara 2, Inpara 3, Inpari 32 and many others. Previously, Fahmi et al. [34] also have been released 11 high yielding rice varieties that suitable for tidal swamp area, especially for acid sulphate soil. Those varieties were Mahakam, Kapuas, Lematang, Sei Lilin, Banyuasin, Lalan, Batang hari, and Dendang.
Adoption of rice crop in acid sulphate soils increases the pH of soil and thus reduces the iron and aluminium toxicity. Several dry food crops like upland rice, peanut and soybean are somewhat tolerant especially on higher topography such as land type C or D [2]. For severe acid sulphate soil, local varieties such as Siam, Jalawara, Talang and Bayur are preferable since it is more tolerant compare to high yielding varieties. Perennial crops that adapted to acid condition such as sago palm, oil palm and coconut are preferable.

4. Conclusions
Land use planning preceded by site characterization with detailed engineering design is the first step to mitigate the effects of pyrite oxidation. Mapping of soil containing pyrite layer depth and controlling the ground water level above that soil layer can prevent oxidation processes. Pyrite oxidation in reclamation tidal land with acid sulphate soil is unavoidable due to drought or over drained. Mitigation efforts for acidified soil can be using water management technologies, amelioration, fertilization and using adapted crops. Among all of mitigation measures, proper water management and amelioration are the most important. These efforts may increase pH and neutralize toxic elements that directly affect to crops productivity. The one-way flow system water management was more effective to reduce toxic element from root zone compared to another. Liming is the most common practices in ameliorate acid sulphate soil. Applying 0.5 to 2.0 t ha$^{-1}$ of lime can increase soil pH and significantly improve plant growth and productivity. Fertilization is needed since ASS low in nutrient status due to intensive leaching and fixation.

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