

Degraded Paddy Soils. I. Theoretical Analysis on the Sulfide Formation and the Effect of Iron Hydroxide Upon Removal of Sulfide from Solution.

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Introduction

There have been a number of works concerning the degraded paddy soils (1,5,6,8,9,11,13). The causes of brown spot of rice, which commonly occurs on rice that grows on degraded paddy soils, has been known to be due to several factors (1,4,9,13). One of which that is supposedly major factor in many Southeastern Countries is the sulfide poisoning.

Sulfate-containing ammonium sulfate had long been a customary nitrogenous fertilizer in some of these countries until somewhat forms of commercial nitrogenous fertilizers became available since the second world war. The continual use of ammonium sulfate caused gradual accumulation of less absorbed sulfate in paddy soils, and this sulfate is converted into sulfide as the soil condition becomes highly reduced during growth period of rice due to high temperature, abundant organic materials that are good energy source for microorganisms and waterlogging which prevents the rapid diffusion of oxygen from the atmosphere to soils.

The sulfide was known to be toxic to rice root, and if the rice root is injured by the excessive sulfide in soil solution the rice root can not meet the nutritional needs of upper parts, thereby rendering the plant to be susceptible to brown spot. The rice affected by brown spot was known to give approximately halved yield of that grown without it.

The application of iron oxide and hydroxide

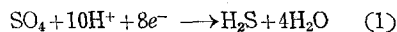
or iron-rich foreign soils to degraded soils was known to be effective in preventing brown spot since the iron can form insoluble sulfides with the sulfide ion thereby reducing the sulfide concentration in the soils (5,7,0,10,12)

The application of ammonium chloride as major nitrogenous fertilizer to paddy soils has been shown to be effective in preventing the brown spot because the fertilizer does not contain sulfate (2)

Although the means with which the sulfide poisoning can be reduced have been proposed, not many theoretical analyses of the sulfide formation under various soil conditions has been published. The present paper deals with the effect of pH upon sulfide formation and the conditions for removal of sulfide from soil solution. The role of iron hydroxide was also presented.

Theory

Sulfate ion can be reduced to sulfide as a medium becomes highly reduced state. The reaction can be written as



There has been no kinetic work concerning the conversion. Many intermediately reduced states of sulfur might be formed, however, no such materials will be taken into consideration in this discussion. If Nernst equation is used for description of the reaction, it becomes

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(\text{SO}_4^{=})(\text{H}^+)^{10}}{(\text{H}_2\text{S})} \quad (2)$$

where E : oxidation potential
 R : gas constant
 T : absolute temperature
 n : number of electrons involved
 F : Faraday

The value of E° for the reaction is -0.303 volts (3).

To solve the concentration of the sulfide at various pH and E, following symbols were conventionally defined.

$$a = (\text{H}_2\text{S}) + (\text{HS}^-) + (\text{S}^{2-})$$

$$b = a + (\text{SO}_4^{2-})$$

$$(\text{H}_2\text{S}) = \frac{b(\text{H}^+)^{10} \cdot 10^{\frac{E+0.2505}{0.0075}}}{\left\{ 1 + (\text{H}^+)^{10} 10^{\frac{E+0.303}{0.0075}} + (\text{H}^+)^9 10^{\frac{E+0.2505}{0.00075}} \right\}} \quad (3)$$

$$(\text{S}^{2-}) = \frac{b(\text{H}^+)^8 \cdot 10^{\frac{E+0.1455}{0.0075}}}{\left\{ 1 + (\text{H}^+)^{10} 10^{\frac{E+0.303}{0.0075}} + (\text{H}^+)^9 10^{\frac{E+0.2505}{0.00075}} \right\}} \quad (4)$$

In most paddy soils, the total sulfur content if expressed in term of moles per liter assuming all the sulfur present in top 20 cm of the soil is uniformly distributed in flooded water becomes around 10^{-3} M. If this value is substituted in place of b in eq. (3) and (4), and (H^+) is expressed as $10^{-\text{pH}}$, the equations become

$$(\text{H}_2\text{S}) = \frac{10^{37.3-10\text{pH}}}{10^{-133.3E} + 10^{40.3-10\text{pH}} + 10^{33.4-9\text{pH}}} \quad (3a)$$

$$(\text{S}^{2-}) = \frac{10^{16.4-8\text{pH}}}{10^{-133.3E} + 10^{40.3-10\text{pH}} + 10^{33.4-9\text{pH}}} \quad (4a)$$

The drawings of eq. (3a) and (4a) are shown in Figure 1 and 2. In both figures, the ordinate represents the oxidation potential of the solution and the abscissa represents pH. Some of the equi-concentration lines for formed H_2S and S^{2-} are drawn in the figures.

From Fig. 1, it is seen that the conversion of SO_4^{2-} to H_2S can take place at relatively oxidized state if pH of a medium is more acid than which has relatively high pH. As pH of a medium increases, the required degree of reduction to effect the conversion of SO_4^{2-} to H_2S increase. It can be said that the conversion line for the reaction can be approximated with

In defining b, it was assumed that the total sulfur present in paddy soils is in the forms of most oxidized, sulfate, and reduced, sulfide, only. No other forms was assumed to be present in the soils.

The ionization constants for H_2S and HS^- are (3)

$$\frac{(\text{HS}^-)(\text{H}^+)}{(\text{H}_2\text{S})} = 10^{-7} \quad \frac{(\text{S}^{2-})(\text{H}^+)}{(\text{HS}^-)} = 10^{-14}$$

If all the known relationships are substituted into eq. (2), and (H_2S) and (S^{2-}) are solved, then

that of H_2S concentration of 10^{-16} in the figure—Starting vertically upwards from the line, i.e. as a medium becomes more reduced, the H_2S concentration increases tremendously. On the other hand, below this line no sulfide is formed, and the majority of the soil sulfur exists as sulfate without being converted into sulfated into sulfate.

It is also interesting to note that the equi-concentration line turns straight upward at particular pH. The left side of this straight vertical line, the low pH, has high concentration of H_2S , where as right side of the line has low H_2S concentration. The decreasing H_2S concentration by passing the vertical line from left to right to within certain extent until it meets the extrapolated line of its own non-vertical portion does not mean that conversion of SO_4^{2-} to H_2S is decreased. Instead, this effect is caused by dissociation of formed H_2S into HS^- or S^{2-} because of increasing pH. Generally speaking, the maximum H_2S concentration which is almost equivalent to 10^{-3} , the total sulfur concentration present in the soil, can be easily attained if pH of a soil is low and reduced condition develops. As pH of a soil increases, not

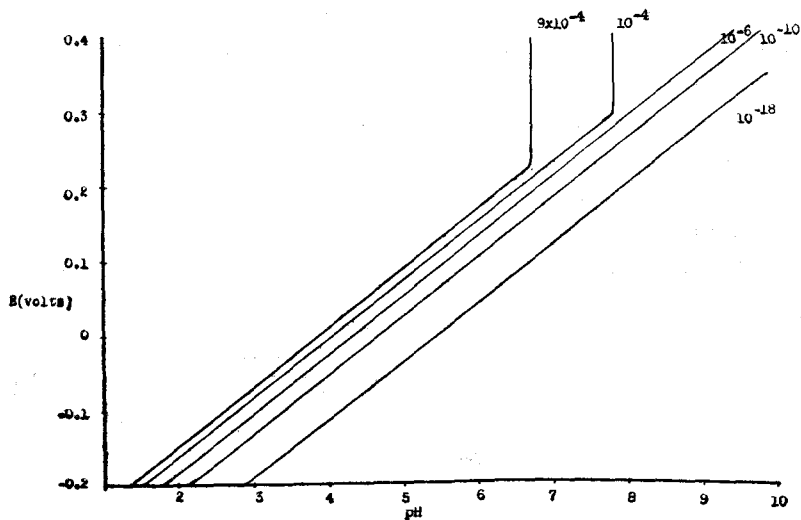


Fig 1. Concentration of H_2S at various pH and E if the total concentration of sulfur is $10^{-3}M$

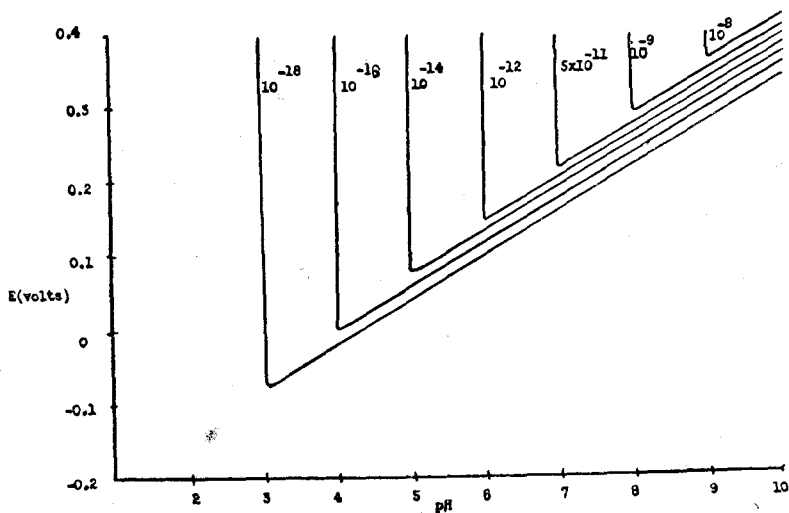


Fig 2. Concentration of S^{2-} at various pH and E if the total concentration of sulfur is $10^{-3}M$

only the formation of H_2S from SO_4^{2-} requires correspondingly more reduced condition but also the formed H_2S dissociates into HS^- or S^{2-} , thereby H_2S concentration decreases.

Figure 2 shows the sulfide ion concentration at particular pH and oxidation potential of a medium. Without the presence of H_2S , S^{2-} does not exist in solution. As a result, the S^{2-} concentration follows the same pattern as H_2S so

far as the formation of it from sulfate is concerned. However, the S^{2-} concentration increases with pH while the reverse was true with H_2S . This is fairly obvious because S^{2-} is formed from H_2S as the result of dissociation.

It should be noticed from Figure 1 and 2, that, at low pH, the formation of H_2S from SO_4^{2-} can readily take place even under relatively oxidized state but the concentration of S^{2-} is

almost none, the majority being H_2S . On the other hand, at high pH, the formation of sulfide is not as easy as that can happen at low pH, whereas much of the formed sulfide presents as $S^{=}$.

It was generally known that in highly acidic solution Fe^{+++} can be converted into Fe^{++} by introducing H_2S . In this reaction H_2S reacts as reducing agent. In natural soils the presence of Fe^{+++} together with H_2S seems doubtful because gradual development of reduced state might have converted all the Fe^{+++} or readily soluble ferric compounds into ferrous ions before any trace of sulfide can form. From this consideration the precipitation of sulfide as ferric sulfide seems improbable, instead the precipitation as ferrous sulfide seems quite obvious. The ferrous sulfide has following solubility product

$$(3). \quad (Fe^{++})(S^{=}) = 3.9 \times 10^{-19} \quad (5)$$

Therefore

$$(Fe^{++}) = \frac{3.9 \times 10^{-19}}{(S^{=})}$$

If the value of $(S^{=})$ from eq. (4a) is substituted into eq. (5), then

$$(6) \quad (Fe^{++}) = 10^{-133.3E - 34.8 + 8pH} + 10^{5.5 - 2pH} + 10^{-1.4 - pH}$$

The equation (6) signifies the allowed maximum Fe^{++} concentration under particular pH, E and total sulfur content of $10^{-3}M$ before precipitation of FeS can take place.

The drawings of eq. (6) for several pH values are shown in Figure 3. The figure is similar to Fig. 2 except the iron content to give precipitation as FeS decreases with increasing pH.

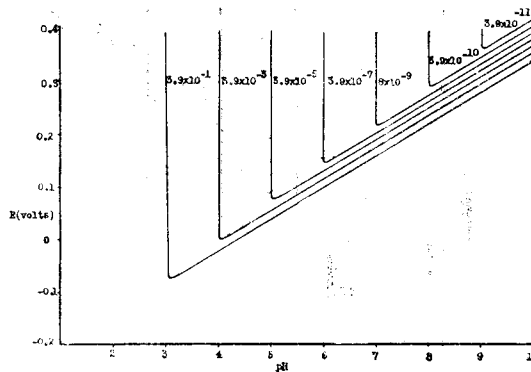


Fig 3. The maximum allowable concentration of Fe^{++} before precipitation as FeS at various pH and E if the total sulfur concentration is $10^{-3}M$

The theory discussed so far does not include any mechanism of the reactions. Only the thermodynamic principle was presented. The sulfide toxicity has received much attention, however, no answer as to what form of sulfide, H_2S , HS^- or $S^{=}$, actually is the most toxic of all has been given. Whatever may be the toxic form, it is generally assumed that the total sulfide concentration may be important and that the toxic effect is proportional to the co-

ncentration.

The toxic effect of sulfide to rice, therefore may be reduced whenever there is low sulfide concentration in a medium. This can be done only if the state of reduction is not severe and also there is no conversion of sulfate to sulfide. Under field condition, however, reduction can occur so often that no natural mean can prevent the development.

A careful examination of Fig. 1 and 2 indi-

cates that there is a certain reduced state from which the sulfide formation starts to take place if a condition develops to a more reduced state. The sulfide formation line which was arbitrarily assigned to $(\text{H}_2\text{S})=10^{-18}$ in Fig. 1 is not parallel to the horizontal axis. In another word the formation of sulfide from sulfate becomes increasingly difficult as pH of a medium becomes basic. This fact has some important consequence since it might refer to the resistibility of a soil to the conversion of its own sulfate to sulfide. The application of lime to soil, therefore, might be effective, to a certain extent, in preventing the formation under moderately reduced state.

From Fig. 2 it is seen that the formed $\text{S}^{=}$ concentration increases with pH. The result if combined with that obtained from Fig. 3 brings out significant consequence. According to an interpretation, the removal of toxicity due to sulfide can readily or easily be obtained if a soil's pH is high. Under acid condition, the majority of the formed sulfide exists as H_2S which may not react with reduced Fe^{++} and accordingly present as dissolved H_2S . This dissolved H_2S may exceed the toxic concentration depending upon how much sulfur was originally present in soil. It should also be pointed out that the iron concentration should really be great enough at this low pH range to effect the precipitation as ferrous sulfide.

As pH of a soil increases, the required ferrous ion concentration to cause the removal of sulfide from solution decrease. The argument brings out conclusion that the application of lime to soil may be effective in preventing the sulfide toxicity.

Another important point to be considered is a comparison between iron-rich and iron-poor soils. For any media containing iron the development of reduced state causes the reduction of ferric form into ferrous form even before any trace of sulfide is formed. This is seen from the values of standard oxidation potential. As the ferric state is reduced, the solution sh-

ould show increase in pH. The degree to which the pH of the solution changes from initial state to the final reduced state may greatly vary depending upon the total readily reducible iron content and initial pH of a soil. Higher the iron content and initial pH the degree of pH increase will be great after reduction. However, if a soil has low iron content and also has low pH initially, the pH change after development of reduction may not be significant. The above argument if expressed in a different way, means that the path of the development of reduction in a soil with certain initial pH does not follow direct upward path from the initial pH in Fig. 1 and 2. Instead, the path for the process may be somewhat leaned toward high pH side as the reduction proceeds. The slope of the path will be small for the high-iron soil while the path will be almost vertically straight for low-iron with low pH soil.

Since the pH naturally increases as the reduction proceeds, the readiness of the precipitation of FeS will be increased depending upon the initial iron content and pH, and this, in turn, accelerates the detoxication of sulfide depending upon the values. The application of iron compound alone sometimes shows a curdiness of brown spot and this might be due to above-mentioned argument. According to the theory discussed, the application of iron compounds with lime may be even more effective.

Summary

The formation of sulfide from sulfate has been discussed from the thermodynamic principles. No mechanism of the reaction has been presented.

From the stoichiometric and Nernst equations for the conversion of sulfate into sulfide, it was concluded that the formation of sulfide from sulfate can take place more readily if pH of a medium is low. The difficulty of this conversion increases with increasing pH.

As pH of a medium increases, the degree of dissociation of H_2S into $\text{S}^{=}$ increases and this,

in turn, renders the chance of precipitation of sulfide as FeS easier.

Higher the pH of a soil or medium, greater is the S^{2-} concentration. The concentration of ferrous ion required to remove dissolved sulfide in a medium by forming insoluble FeS decreases with increasing pH.

From the theory it was pointed out that an application of lime and iron rich foreign substances to a soil may be effective in causing the removal of dissolved sulfide from solution.

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