PHYSICOCHEMICAL RELATIONSHIPS OF SELECTED IRON AND SULFUR SYSTEMS IN SUBMERGED SOILS AND THE POSSIBLE OCCURRENCE OF H_2S TOXICITY

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Chong Woon Hong

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Boyd G Ellis
Major professor

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ABSTRACT

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The assumption was made that in submerged paddy soils the activity of Fe^{++}, which controls the activity of H_2S, might be determined by the system $FeCO_3$-H_2O-CO_2. Using the solubility constant of $FeCO_3$ and the dissociation constants of H_2CO_3, an equation defining the pH-pFe^{++} relationships was derived: $pFe^{++} \cong 0.5\ pH + 0.3$. From this, another equation which defines the pH-pH_2S relationships in the system $FeCO_3$-FeS-H_2O-CO_2-H_2S was also derived: $pH_2S \cong 1.5\ pH - 2.86$.

Experiments with synthetic $FeCO_3$-H_2O-CO_2 and $FeCO_3$-FeS-H_2O-CO_2-H_2S systems proved the validity of these two equations. In reduced paddy soils it was found that pH-pFe^{++} relationships were reasonably close to those of $FeCO_3$ systems.

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The experimentally obtained pH-pH_2S and pH-pE relationships among Fe systems prepared by alkalizing FeS-contaminated solutions containing varying ratios of Fe^{3+} and Fe^{++} suggested that the occurrence of ferrousferric hydroxide($Fe_3(OH)_8$) was unlikely below pH 7.0. The investigation of pH-pH_2S and pH-pE relationships in reduced soil systems revealed that the reduced soils contained the system iron oxides $FeCO_3$-FeS-H_2O-CO_2-H_2S, rather than the system $Fe_3(OH)_8$-FeS-H_2O-CO_2-H_2S suggested by previous workers.

A survey of the activity of H_2S in 194 soil samples representing major Korean paddy soils disclosed that the activity of H_2S from pH 6.0 to 7.0 ranges from $10^{-6.18}$ to $10^{-7.68}$ mol/l. These concentrations would suggest that there is a remote possibility of H_2S toxicity occurring in most Korean paddy soils.

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Finally the author wishes to express his profound gratitude to his mother and his wife, Moon Sook, for their unselfish sacrifices and encouragement.

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INTRODUCTION

The problems of hydrogen sulfide toxicity on lowland rice (*Oriza sativa*) have been studied extensively, especially in the oriental countries where rice is the major food crop. Because it has long been assumed that the hydrogen sulfide toxicity is one of the major causes for the occurrence of akiochi disease or the autumnal declination of rice which depresses crop yields substantially, extraordinary research efforts have been undertaken to solve this problem.

Earlier workers have generally agreed that insufficiency of active Fe in a paddy soil can be associated with the occurrence of hydrogen sulfide toxicity. They reasoned that in such a soil, the sulfide produced during the course of reduction might remain as free hydrogen sulfide due to insufficient amounts of active ferrous iron which would inactivate the sulfide by forming sparingly soluble iron sulfide. Consequently, they suggested that the enrichment of a paddy soil with active Fe could be one of the principal means for minimizing the hazard of hydrogen sulfide toxicity.

This idea has been widely accepted for a long time without being thoroughly investigated on a scientific basis. Recently, however, this long-time accepted principle has come under serious criticism because of increased knowledge of the complex physicochemical characteristics of waterlogged soils. Especially vulnerable to criticism has been the lack of quantitative evidence and erroneously selected diagnostic criteria in previous workers' investigations of this problem.

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With few exceptions, earlier scientists believed that the higher the content of active Fe in a paddy soil, the less the possibility of occurrence of hydrogen sulfide toxicity. However, only a few of them tried to identify and to relate the critical levels of active Fe in a soil below which hydrogen sulfide toxicity would occur. Even today, reliable information on the threshold concentrations of hydrogen sulfide which would be toxic to rice plants under field soil conditions are extremely limited. It appears that earlier workers have considered the problem of hydrogen sulfide toxicity in a broadly qualitative sense.

Attempts to relate the level of active Fe in the soils as the diagnostic criterion for the incidence of hydrogen sulfide toxicity has proved unreliable. The activities of hydrogen sulfide in the reduced soil systems are determined by the activities of ferrous iron in association with the other physicochemical characteristics of the system. The level of active Fe estimated from air-dried soil samples by the use of strong reducing agents usually does not provide any reliable information on the activities of ferrous iron and the other factors influencing the activities of hydrogen sulfide in the reduced soil systems.

These discrepancies are now recognized by a number of investigators who recently have attempted to characterize the quantitative aspects of the occurrence of hydrogen sulfide in reduced soil systems by direct investigations of the reduced soil system itself. Some investigators have tried to identify the activity of hydrogen sulfide as a function of such factors as the activity of ferrous iron, pH, Eh and etc. In defining the functional relationships, the principles of physical chemistry must be fundamentally applied. On the other hand, some researchers have attempted the direct measurements of hydrogen sulfide _in situ_ or in soil solution.

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These efforts have resulted in major advancements in our understanding of the quantitative aspects of hydrogen sulfide in waterlogged soils. However, there are still many problems in coordinating the theoretical principles with applied research data. It has been observed that there are substantial discrepancies between the theoretically predicted values and the actual measured data for the activity of hydrogen sulfide in the reduced soil systems. The causes for these discrepancies have not been properly investigated.

The overall objective of the present study was to examine the validity of assumptions and results of previous investigations which have attempted to define and resolve the problem of hydrogen sulfide toxicity on lowland rice. In view of our present knowledge of the physicochemical characteristics of soils under reduced conditions, the specific objectives of this study were: (1) to investigate the theoretical relationships among pH, Eh, activity of ferrous iron and activities of hydrogen sulfide under the respective systems of FeS - H_2O - H_2S, $FeCO_3$-FeS-H_2O-CO_2-H_2S, iron oxide - $FeCO_2$ - FeS - H_2S - CO_2 - H_2O, iron hydroxide - $FeCO_3$ - FeS - CO_2 - H_2S - H_2O, and in the reduced soil systems; (2) to test the validities of the theoretical findings; and (3) to obtain the practical information on the occurrence of hydrogen sulfide in major Korean paddy soils.

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REVIEW OF LITERATURE

A. Hydrogen Sulfide Toxicity on Lowland Rice

1. Debut of the Problem

According to Engler (1972), Sturgis (1936) gave the first published evidence of the harmful effect of H_2S. However, Osugi and Kawaguchi's (1938) work has widely been cited as the earliest study on the toxicity of hydrogen sulfide on lowland rice. They made a detailed study on the "root rot" disease of rice occurring in a poorly drained sandy soil. In the field they observed that when the soil under water was pressed, a vigorous bubbling of gases occurred. They did not remark on the composition of the gases accumulated in the soil. Instead, with the soil samples taken from that site they conducted some experiments on the formation of sulfide under waterlogged condition. After a certain period of incubation, soil was analyzed for sulfuric acid extractable sulfide. From these studies they concluded that the hydrogen sulfide might be a principal cause for the "root rot" disease of rice.

2. Conditions for the Occurrence of H_2S Toxicity

Osugi and Kawaguchi (1938) made the presumption of H_2S toxicity upon the basis of their studies on the formation of sulfide (acid extractable) in the soil. Since it is true that the amounts of the acid extractable sulfide cannot be a quantitative clue for the activity of H_2S in the soil, it may be pointed out that their conclusion was made with misleading logic.

Shioiri (1948), in discussing the chemical characteristics of paddy soils, emphasized the importance of free iron oxide in the soil. He

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pointed out that in the degraded paddy soils where the akiochi, helminthosporium disease and the root rot of rice habitually occured, the free iron oxide was severely leached from the top soils. According to him, the rice roots in such soils are a white or blackish color, in contrast to the reddish-brown color of the roots in the soils containing abundant free iron oxide. He attributed the whitening or blackening of the rice roots to the failure of soils in depressing the activity of sulfide. This remark has been appreciated as of great significance, because it gave the logical clue to the concept that the presence of sulfide is not the complete condition for the occurrence of H_2S toxicity. The sulfide should exist as free hydrogen sulfide to be toxic.

Kumada (1948) clarified the fact that harmful sulfide is free H_2S not the combined sulfide, by finding that the inculsion of iron sulfide (FeS) in culture solution did not harm the rice plant while H_2S affected the growth of rice detrimentally.

Shioiri and Yokoi (1949) suggested a mechanism for the degradation of paddy soils with special reference to the leaching loss of free Fe from the top soils. They mentioned that the contact of sulfide with ferric iron would result in the reduction of Fe, producing iron sulfide (FeS) and that the iron sulfide produced in such a manner, in the presence of excess sulfide, would be peptized and liable to leaching. Shioiri and Yoshida (1951) tried to explain the leaching of Mn on the similar principle: manganese oxide would be reduced by sulfide to yield manganese sulfide and the manganese sulfide would be peptized and become easily mobile. As the result of these studies, it has been believed that the addition of S to soils via application of fertilizers may bring forth the hazard of H_2S toxicity, and at the same time result in the acceleration of the degradation of paddy so

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Information on the critical level of active Fe necessary to check the production of H_2S at high concentration is not abundant. Shiga (1962) suggested the level of 0.2% of active Fe as the threshold concentration. Park (1967) reported, with Korean paddy soils, that pH value of below 6.0 and active Fe content of below 0.3% are the conditions necessary for detectable amounts of free H_2S in reduced soils.

These figures for active Fe contents, however, cannot be of universal applicability. The activity of H_2S in reduced soils is determined by pH and the activity of ferrous iron as the following equation shows:

$$pH_2S = 2pH - 2.56 - pFe^{++}$$

where $pX = -\log X$.

Thus the conditions for the occurrence of H_2S should be defined on the basis of chemical characteristics of reduced soils.

Bloomfield (1969) and Bloomfield and Pruden (1962, 1967) have reported that even in the presence of enough active Fe, free H_2S evolved from reduced soils. They speculated that the important factor is the activity of ferrous iron in the reduced soil systems, not the total amounts of active Fe in soils. Kumada (1950) and Sato and Yamane (1959) observed that in soils unusually high in organic matter, the incorporation of active Fe did not check the evolution of H_2S effectively. They speculated that in such systems the Fe could be inactivated by organic matter, allowing the sulfides to remain as free H_2S. Thus it may be pointed that the previous workers have been using incorrect criteria for the judgement of the possibility of the occurrence of H_2S toxicity.

3. Plant Physiology of H_2S Toxicity

The problem of H_2S toxicity had been grasped only in terms of assumption until plant

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Mitsui and co-workers (1951), in a preliminary study on the effect of H_2S on rice, found that the contact of rice roots with a solution containing as low as 0.07 ppm of H_2S for 90 hours caused the wilting of young rice seedlings. In further studies with solution culture of rice at 2 ppm of H_2S treatment, they observed that the presence of H_2S caused remarkable depressions in the absorption of nutrients and water by rice plants, P and K being most significantly affected and Mg and Ca least affected. The absorption of silica and N were also moderately depressed.

Baba and co-workers (1952) in studying the nutritional physiology of rice in connection with the incidence of the helminthosporium disease, confirmed the findings of Mitsui and co-workers. By including 10-20 ppm of H_2S in their culture solutions, they observed the reduction of nutrient absorption by rice, the degree of reduction for individual nutrients being in the order $K > N(NH_4^+) > Mn > H_2O > Ca > P$. Their results are similar to the findings of Mitsui and co-workers, with the exception of P. Further, they also reported that H_2S not only affected the nutrient uptake of the rice plant, but also retarded the synthesis of protein by inhibiting the aerobic respiration of the plant.

Okajima and Takagi (1953a) confirmed the detrimental effect of H_2S on the accumulation of nutrients by rice. At the same time they (1953b) found that under the influence of H_2S in culture solution, the synthesis and translocation of carbohydrates in rice plants were depressed. In their subsequent studies (1955) on the effect of H_2S on the respiration of rice roots, they observed a remarkable decrease in O_2 consumption and CO_2 production by excised rice roots taken from plants pretreated with around 10 ppm of H_2S for 24 hours.

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Apart from the aspects of nutrition, Mori (1954) studied the morphological characteristics of rice roots under the influence of H_2S. Addition of H_2S, at the rate of 2.3 cc of H_2S-saturated solution in a liter of culture solution, induced the development of lateral roots and decreased both the number and the length of roots.

4. The Critical Concentration of H_2S for Toxicity

By the aforementioned efforts, the fact that H_2S is harmful to rice has been demonstrated definitely. However, in spite of the continued efforts by many scientists, widely acceptable information on the critical concentration of H_2S which can be toxic to rice plants in practical field soils has not emerged.

To know that H_2S is harmful to rice may not be enough for the assessment of H_2S toxicity in practical field soils. Information on the critical concentration of H_2S and on the possibility of the occurrence of H_2S at the critical concentration or beyond in practical soils is essential to rpove the occurrence of H_2S toxicity in field soils.

Although 0.07 ppm of H_2S was suggested by Mitsui and co-workers and has been cited widely by many investigators as one of the possible critical concentrations (Ponnamperuma, 1955; Hollis, 1967; Yamane, 1967; Pitts, 1971; Allam and Hollis, 1972; Engler, 1972; and Ayotade, 1972) , this value does not seem to be of wide applicability.

As mentioned before, earlier workers with few exceptions would use around 10 ppm or higher concentration of H_2S in culture solutions to demonstrate toxicity. Baba and co-workers (1965) cited unpublished data of Inada, who found that the addition of 10-20 ppm of H_2S to the culture solution did not bring forth any abnormal symptom in the rice. Tanaka (1968) also reported that inclusion of 1-10 ppm H_2S in culture solution

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did not harm the rice plant seriously. Both workers concurred that rice plants were damaged only when the culture solution contained both H_2S and ferrous iron simultaneously.

Shiga (1962) tried to correlate the concentration of H_2S under actual soil conditions with the performance of rice plants. In a series of pot experiments he found that 3 ppm of H_2S, measured at 45 days after transplanting, did not affect the grain yield; 5-10 ppm resulted in a 10% yield decrease; 20 ppm or more resulted in death of the rice. Yamane and Sato (1961a) could detect as much as 3-7 ppm of H_2S in some muck soils under field conditions. But they observed no symptoms of toxicity on the rice roots.

Allam and Hollis (1972) conducted a quantitative study on the effect of H_2S on the activities of various enzymes, such as cytochrome oxidase, catalase, peroxidase, ascorbic acid oxidase and polyphenol oxidase, in 15 day-old rice seedlings separated from culture media (vermiculite), then pretreated with H_2S by immersing the roots in solutions containing concentrations of 0.1-3.0 ppm H_2S. They could demonstrate significant inhibition of the activites of enzymes by H_2S at all of the tested concentrations.

Between the findings of Mitsui and Allam with their co-workers and the experimental results obtained by Baba, Tanaka, Shiga and their collaborators, there is a large difference in the concentration of H_2S considered to be toxic. It is interesting to note that the former group of workers gave the H_2S treatment to very young rice seedlings under conditions of discontinued supply of nutrients, while the latter group introduced the H_2S into culture solutions which contained all of the necessary nutrients and in which rice was actively growing. It may be

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that the rice plant actively growing in the nutrient solution would show greater tolerance to toxins than the very young plant under discontinued nutrient supplies.

From this light, it would be reasonable to take account of the findings of later groups in exploring the practically applicable critical concentrations of H_2S for toxicity since field soils contain many interacting components in addition to water and H_2S. In this sense, the experimental results of Shiga (1962), and the findings of Yamane and Sato (1961) seem to be more realistic.

5. Major Physiological Diseases of Rice and H_2S Toxicity

Akiochi (autumnal decline; Japan and Korea), akagare (red wilt disease; Japan), bronzing (tropical areas), suffocation (China), bruzone (Hungary) and straighthead (U.S.A.) are the physiological diseases of rice which are known to have some connection with H_2S toxicity, directly or indirectly.

(a) Akiochi

In earlier days, akiochi had been believed to occur mostly on degraded paddy soils where H_2S toxicity might occur. However, along with advancements in understanding the disease, it has come to be believed that it is mainly due to shortage of nutrients at later growth stages of rice.

Baba *et al*. (1965), in reviewing the causes of akiochi disease, put the malnutrition of later growth stages of rice in first place. They mentioned N deficiency secondly and root injury and inhibition of nutrient uptake thirdly.

The general symptoms of akiochi have been described: "The plant shows vigorous and normal growth in early stages, and it is expected to give high yield. However, at later stages the plant begins to decline, with death of lower leaves resulting in a shabby appearance, and the yield of rice is unexpectedly

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From the symptoms, it sounds reasonable to attribute the akiochi of rice to the failure of soils to continue the supplying of nutrients. Generally, degraded sandy soils are unusually low in both nutrient holding capacity and buffering capacity. In such a soil, the application of fertilizer at the time of transplanting would render high concentrations of fertilizer in soil solution resulting in vigorous growth of the plant at early stages. At later growth stages, due to the poor nutrient holding capacity of soil, if repeated topdressings of fertilizer are not made, desirable nutrient supply to the plants would be discontinued; accordingly, plant growth would be checked. What makes the situation worse is the vigorous growth at early stages. A vigorous plant standing on a soil with poor nutrient supply can suffer serious nutrient deficiencies.

This point of view is supported by experimental results obtained by Baba and Harada (1954) and Baba (1958) which were summarized by Baba et al. (1965) as follows: "When rice is grown under a nitrogen deficient condition throughout the whole growth period, no akiochi occurs, but when it is grown with an excess of nitrogen at the early growth stage and then subjected to a deficiency of nitrogen in later stages, akiochi occurs".

Nitrogen is not the only element that is deificient in degraded paddy soils. Potassium, silica and Mn have been reported to be low in akiochi-affected rice plants (Susuki and Maeda, 1948; Park et al., 1964; Park, 1967). Akiochi, according to Takijima (1963), also occurs on poorly drained, peaty soils. After intensive studies on the poor performance of rice on poorly drained peaty soils, he concluded that the accumulation of some microbial metabolites such as CO_2, organic acids and unidentified organic substances may play major roles in damaging the rice roots. He maintains

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that rice roots damaged by microbial metabolites are very liable to the intrusion by Fe^{++} and sulfide. However, he offered no remarks on the forms of sulfide that intrude rice roots. In his studies, sulfide was analyzed by extracting the soil or rice roots with 2N H_2SO_4, and he mentioned that the concentration of free H_2S was very low.

(b) Akagare

A thorough review on the problem of akagare was made by Baba, Inada and Tajima (1965). Akagare is characterized by the occurrence of reddish brown spots on older leaves of rice at early growth stage. An associated acute symptom is the death of leaves from the tips. This disease also occurs under unfavorable soil conditions. Depending on the symptoms and causes, the disease has been classified into three distinct types, I, II and III (Baba _et al_., 1965). Among three types of akagare, type II has been known to have some connection with H_2S. Yamaguchi and co-workers (1957), through a survey of soils on which akagare disease occurred frequently, concluded that those soils were characterized by (a) low K supplying power, (b) abundant easily decomposable organic matter, (c) evolution of H_2S, (d) low active Fe, (e) excess of ferrous iron, and (f) intensive reduction of soil. From this information, it can be pointed out that it is not a single factor that causes the incidence of akagare (type II). H_2S seems to be one of the soil metabolites which can depress the activity of rice roots, resulting in unbalanced nutrient uptake. From this point of view, the work of Baba _et al_. (1955) merits appreciation. They could demonstrate the incidence of akagare in rice by withdrawal of potassium application and by application of lactic acid to the soils.

(c) Bronzing

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Indonesia, "Penijakit merah" and "brown disease" in Ceylon. Ponnamperuma (1955) describes the symptoms of this disease as a "stunting of growth, a reddish discoloration of the older leaves followed by a pronounced marginal scorch, curling and death of the leaves, a damaged root system, and poor panicle and grain development".

On the causes of the disease there has been some disagreement among investigators. Ponnamperuma (1955) suggested that excess soluble iron (Fe^{++}) is the most probable causative factor for the disease. He (1958) demonstrated through a pot experiment that excess ferrous iron in soil solution under reduced conditions has a direct connection with the occurrence of the disease. In the same experiment he showed that by depressing the concentration of ferrous iron in soil solution with an application of lime, the disease could be checked effectively.

Baba _et_ _al_. (1965), in reviewing the physiological diseases of rice, presented the view that an excess of Fe could not be the single cause for the occurrence of bronzing. As references supporting their view, they cited Ota and Yamada's (1962) findings and Inada's unpublished data.

Ota and Yamada (1962) found that the free Fe content of a sandy soil in which severe bronzing was observed, was significantly lower than that of a boggy soil free from the disease. Inada (1962) also found that the addition of ferrous oxide to a healthy soil to increase the Fe content as much as 0.6% on dry soil basis did not induce the disease. These findings, however, do not seem to provide a logical ground to criticize the view that bronzing is caused by Fe toxicity.

Ponnamperuma (1958), in discussing the possibility of Fe toxicity, mentions the concentration of Fe^{++} in soil solution of reduced soil systems (intensity factor), while Ota and Yamada (1962), and Inada (1962) mention the

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mention the amounts of active Fe in the soil (capacity factor). The amounts of active Fe are not usually correlated with the activity of Fe^{++} in soil solution.

Certainly it is of unusual interest to notice that the more the active Fe content in a soil is, the less is the possibility of the occurrence of Fe toxicity. The following considerations provide explanations for this point:

$Fe_2O_3 + 6H^+ + 2e = 2Fe^{++} + 3H_2O$ . . . . (1)

$Fe^{++} + 2OH^- = Fe(OH)_2$ . . . . (2)

$pFe^{++} = 2pH - 2pkw + pks$ . . . . (3)

Equation (1) implies that the reduction of ferric iron oxide in soil is accompanied by a decrease in soil acidity. The more Fe is reduced in the soil, the higher the pH of the system will be. Equations (2) and (3) indicate that the higher the pH of the system the lower the concentration of ferrous iron in the system. In the equation (3), pX is -logX and kw and ks are the dissociation constant of H_2O and solubility product of $Fe(OH)_2$, respectively. Summing up all of these implications, it is clear that the higher the content of active (reducible) Fe in the soil, the lower the intensity of ferrous iron in the solution of reduced soils. When considered in this way, the aforementioned Ota and Yamada's findings in some sense are another proof for the view point that bronzing is attributable to excess ferrous iron in reduced soil.

Baba <u>et al</u>. (1965) cited the unpublished data of Inada as evidence for the connection of H_2S with the occurrence of bronzing. In brief, Inada's experimental results were interpreted by the reviewers as showing that H_2S added to the culture solution at the level of 10-20 ppm did not induce bronzing; however, H_2S at the same level in combination with 150 ppm of ferrous i

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of ferrous iron enhanced the development of bronzing (at low pH).

Tanaka and co-workers (1968) confirmed Inada's finding through a more refined experiment. They summarized their observations as follows: "Bronzing symptoms developed at 100 ppm Fe (ferrous) with $S^{=}$ (H_2S) levels above 7 ppm, and 300 ppm Fe with $S^{=}$ levels above 3 ppm. Plants at 300 ppm Fe without sulfide remained normal in appearance".

These findings led them to speculate that, when ferrous iron co-exists with H_2S in the soil, H_2S will impair the oxidizing power of rice roots at first step then ferrous iron will move into the plant easily resulting in iron toxicity and bronzing. They pointed out that the co-existence of H_2S and ferrous iron at high concentration might be one of the conditions for the incidence of bronzing.

The co-existence of H_2S and ferrous iron at an appreciably high concentration is no matter of doubt at low pH values (i.e. below 5.0, as in the above mentioned studies). However, at pH values above 6.0, which are commonly encountered in reduced paddy soils, the simultaneous existence of H_2S and ferrous iron at high concentration is unlikely. But Tanaka and co-workers (1968) tried to explore this possibility on a theoretical basis as follows:

In the presence of CO_2 in reduced soil, $FeCO_3$ may be formed. In the $FeCO_3$-CO_2 system the activity of ferrous iron is defined as:

$$pFe^{++} = 2pH - 7.486 - pPCO_2 \quad \ldots\ldots\ldots\ldots\ldots (4)$$

On the other hand, in a FeS-H_2S system the activity of ferrous iron is a function of pH and pH_2S:

$$pFe^{++} = 2pH - 3.56 - pH_2S \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Where $FeCO_3$ and FeS co-exist in a system, the relationship between CO_2 and H_2S can be defined by combining equations (4) and (5) as:

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From equation (6) they maintained that even at neutral pH values, if PCO_2 is high, the activity of H_2S can remain high enough with high ferrous iron concentration, to cause H_2S-induced Fe toxicity.

Their interpretation of equation (6), however, does not seem to be logical. In fact, this equation defines only the relationship between the activity of H_2S and the partial pressure of CO_2. Certainly, equation (6) tells that increased partial pressure of CO_2 would result in increased H_2S activity. But it is also true that increased partial pressure of CO_2 lowers the pH of soil systems (Ponnamperuma _et al_.,1969). If, by any peculiar means, the CO_2 partial pressure is increased without altering the pH (fixing at the neutrality) the activity of ferrous iron should be lowered (equation (4)). Accordingly, the simultaneous existence of ferrous iron and H_2S at such a high concentration as 300 ppm Fe^{++} and 5 ppm H_2S at the neutral pH value is not supported logically, even in the system of FeS-H_2S-$FeCO_3$-CO_2.

Bronzing disease is not confined only to very acid soils. Because the simultaneous presence of Fe^{++} and H_2S at high concentrations is not possible at near neutral pH (above 6.0), the idea of H_2S induced Fe toxicity as the cause of the occurrence of bronzing cannot be applied widely.

(d) Suffocation

Yoshida (1971), in reviewing the nutritional disorders of rice in Asian countries, mentioned that a certain type of suffocation disease occurring in Taiwan is a virus disease. Prior to this, the disease had been recognized as a purely nutritional disorder. The disease is locally referred to as "yellow wilt disease" and is characterized by discoloration of leaves and stunted growth, accompanied by root rot. According to Takahashi

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(1961), the disease resembles the akagare disease observed in Japan.

Studies on physiological behavior and soil chemical characteristics (Lee et al., 1956; Chiu, 1966; Wu et al., 1972) have indicated that the disease has obvious connections with the drastic reduction of soils and the accumulation of reduction products, such as ferrous iron, organic acids, and sometimes Mn^{++}. The diseased plants usually contain less K, and an excess of Fe and Mn.

Wu and her co-workers (1972) noticed the intensive proliferation of certain strains of microorganisms in the diseased soils. After exhaustive efforts, they implicated a particular organism, Pseudomonas putida, Ro. 26. They maintained that this organism reduces sulfate to produce H_2S in the rhizosphere. The H_2S produced in such a manner, in turn, would depress the oxidizing power of rice roots allowing the easy intrusion of ferrous iron into rice roots, resulting in the occurrence of Fe toxicity of K deficiency in rice. However, they did not give any quantitative data on the extent of occurrence of H_2S in such soils.

(e) Bruzone

Vamos (1958, 1959) reported the occurrence of a certain type of physiological disorder seemingly similar to akiochi of rice observed in Japan. With little quantitative information on the evolution of H_2S in soil, he mentioned that the disease is caused by the presence of H_2S in the soil.

Vamos in latter studies (1964) suggested a mechanism by which H_2S penetrates the cell walls of rice roots. He said that sudden cooling of the surface layer of a soil would result in the oxidation of FeS to yield sulfuric acid. Upon the admixing of sulfuric acid and H_2S in lower layers, the latter would reduce the former to SO_2. He speculated that the SO_2

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produced in this manner would damage the rice roots and allow H_2S to penetrate the rice roots easily. Although this idea sounds logical, he has not put forth any quantitative figures to support his points.

A theoretical examination of this idea leads to the conclusion that, though the idea in itself is interesting, the practical significance of it does not seem to be too great:

$$\underset{(-6.54)}{H_2S} + \underset{(-177.34)}{H_2SO_4} = \underset{(-71.79)}{SO_2} + \underset{(0)}{S} + \underset{2(-56.69)}{2H_2O} \;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (7)$$

$$\Delta F^\circ(25^\circ C) = -1.29 \text{ KCal/mol.}$$

$$K = \frac{p(SO2)}{(H_2S)(H_2SO_4)} = 10^{0.94}$$

The ΔF° for the reaction indicates that the reduction of sulfuric acid by H_2S is a spontaneous reaction. Thus, qualitatively, the production of SO_2 by admixing of H_2S and sulfuric acid is possible. However, the value of the equilibrium constant being small, the expected concentration of SO_2 is very low. Even when the value of 10^{-4} M (=3.4 ppm) for H_2S is taken (a very high value for most soils), the partial pressure of SO_2 becomes $10^{-7.06}$ atm., which seems to be too low to be a matter of practical significance.

(f) Straight Head

The straight head disease of rice is characterized by unbending panicles due to the failure of grain development. Although the general cause of the disease in unknown, Atkins (1958) points out that the disease occurs frequently on sandy soils abundant in easily decomposable organic matter, under continuous flooding. This information indicates that the disease might have some connection with the intensive reduction of soils and the accumulation of toxic substances. Conclusive information on the

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connection of this disease with H_2S is scarce. Inada and co-workers (1953), cited by Baba et al. (1965), showed that application of fertilizers without sulfate were more or less effective in preventing the occurrence of the disease. This serves as indirect evidence of the possible influence of H_2S on the straight head disease.

Regardless of the insufficiency of definitive information, some scientists consider H_2S to be a partial causative factor for the straight head disease of rice (Engler, 1972; Ayotade, 1972).

6. Preventive Measures for H_2S Toxicity

Studies on the prevention of H_2S toxicity have been made mainly in connection with the akiochi disease of rice. As mentioned earlier in this review, since Shioiri (1943) emphasized the importance of free iron oxide or active Fe in checking the occurrence of free H_2S, many scientists have focused their efforts to demonstrate the effect of the application of Fe containing materials such as red earth, iron oxide powder, and muds of river or lake basins.

Suzuki and Maeda (1948), in a review on preventive measures for akiochi of rice, pointed out that the application of red earth, manganese sulfate and iron oxide powder and avoiding the use of S-containing fertilizers would be recommendable to escape from the hazard of H_2S toxicity. Araki (1952) in a discussion on the prevention of akiochi, agreed with Suzuki and Maeda. Saheki and co-workers (1952) reported that the addition of a factory by-product which contained 10% Fe_2O_3 and 70% gypsum was effective in increasing the yield of rice on an alluvial soil. In early days, it had been believed that the application of Fe-containing materials on soils susceptible to akiochi should be one of the most sure remedies. However, experimental results obtained afterwards have revealed that, in many cases, the applica

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the application of Fe-containing materials is not so effective as it was expected to be.

Ito (1948), in a study on the effectiveness of applications of red earth and lake basin mud to degraded paddy soils, pointed out that lake basin mud was more effective and that the Fe content of the materials was not related to their effectiveness. He further mentioned that the effectiveness of lake basin mud seemed to be partly due to the organic N it contained.

Hashimoto, Kota and Mitsui (1948) also reported that the application of Fe alone would not be an effective measure for the improvement of degraded paddy soils. They emphasized the importance of the amendment of soils with silica. The importance of the application of silica for the improvement of degraded paddy soils was well demonstrated by Ueda and Kimura (1959). They found that the application of earth derived from serpentine, which was abundant in available silica, together with calcium silicate and magnesium carbonate, was particularly effective in preventing the occurrence of akiochi. Through further survey, Ueda and Yamaoka (1959) urged that the amendment of soil with silica is the most effective practice on degraded paddy fields where soil is derived from granite.

In Korea where akiochi is one of the most serious complaints in the cultivation of rice, many trials have been conducted on the effectiveness of Fe-containing materials, together with silica and other soil amendments. Hong (1972), reviewing experimental results obtained from akiochi suspected fields at as many as 164 locations throughout the country, found that the application of Fe-containing materials did not bring forth any remarkable effects. He noticed that, instead of Fe-containing materials, the application of calcium silicate was much more effective in preventing

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akiochi. The fact that the application of Fe-containing materials to akiochi suspected soils is not effective, makes the reality of the occurrence of hydrogen sulfide toxicity doubtful.

B. Chemistry of Waterlogged Soils

The chemistry of waterlogged soils has been reviewed and discussed extensively by Ponnamperuma (1955, 1965 and 1972a, b), encompassing theoretical principles as well as practical significance.

Waterlogging a soil, in a physical sense, is a rather simple procedure; that is to supersaturate the soil with water and cover it with water at a certain depth. However, the consequences of this simple operation involve many extraordinary features of soil chemistry.

First of all, the oxygen diffusion coefficient of water being very small, the water layer overlying the soil effectively curtails the supply of oxygen to the soil system. When dissolved free oxygen is exhausted by the activities of aerobic microorganisms, the soil becomes devoid of free oxygen (Takai <u>et</u> <u>al</u>., 1956). As time proceeds under this condition, anaerobic organisms proliferate and anaerobiosis prevails in the soil system. Following are some examples of anaerobic oxidations and degradation of organic substrates in waterlogged soils due to the activities of anaerobic organisms:

$$C_6H_{12}O_6 + H_2O \dashrightarrow CH_3COOH + 2HCOOH + C_2H_5OH \text{ . . . . } (8)$$

$$5C_6H_{12}O_6 + 24KNO_3 \dashrightarrow 3CO_2 + 18H_2O + 24KOH + 12N_2 \text{ . . . . . } (9)$$

$$\underset{\text{(cysteine)}}{HS\cdot CH_2\cdot CH\cdot (NH_2)COOH} \overset{H_2O}{\dashrightarrow} H_2S + NH_3 + \underset{\text{(pyruvic acid)}}{CH_3COCOOH} \text{ . . . . . . } (10)$$

Reactions (8), (9) and (10), respectively, are examples of heterofermentation, metafermentation (or anaerobic respiration) (Delwiche, 1967) and anaerobic degradation of amino acids. These are major patterns of anaerobic decc

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decomposition of easily decomposable organic matter in soils.

Heterofermentative reactions result in the accumulation of various types of organic acids observed by many workers (Nitsui et al., 1959; Metemura et al., 1961; Takijima, 1963; Yamane and Sato, 1970). The metafermentative reactions which have been widely known as "anaerobic respiration" are of particular importance, because inorganic oxides with high oxidation states are reduced by these processes. Reduction of nitrate to molecular nitrogen or to ammonia and of sulfate to sulfide are typical examples. Ferric oxides are also known to be reduced by metafermentation (Roberts, 1947; Bromfield, 1954; Kamura and Takai, 1961; Kamura et al., 1963). The anaerobic degradation of protein or amino acids is the major cause for the evolution of ammonia in submerged soils, and the sulfide existing in such soils arises, in part, from these processes.

Thus, anaerobiotic processes are the primary cause for unique characteristics which emerge in waterlogged soils as they become reduced.

The characteristics of reduced soil, as might be expected from the fact that the system is under the profound influence of biological activities, are complicated and involve various textures.

1. Redox Potential of Waterlogged Soils

(a) Significance of Redox Potential

Oxidation-reduction reactions involve the transferring of electrons from one reagent to another. Loss of electrons is oxidation and the reverse is reduction. In an oxidation-reduction reaction, the intensity of electrons or electromotive force (EMF), determines the direction of reaction; the higher the intensity of electrons, the more reduction. For a redox reaction, Ox + ne⁻ = Red, the redox potential is expressed as,

$$E = E^\circ - \frac{Rt}{nF} \ln \frac{(Red)}{(Ox)} \quad . \; . \quad (11)$$

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where, (Red) and (Ox) denote the activities of reductant and oxidants respectively, and E° is the standard EMF or the EMF when the activities of (Red) and (Ox) are 1 molal (Latimer, 1961).

Equation (11) is written as follows when the numerical values for R, T, and F at 25°C are substituted and natural logarithms are converted to common logarithms:

$$E = E^\circ - \frac{0.059}{n} \log \frac{(Ox)}{(Red)} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (12)$$

This equation has been used for a long time. However, Sillen (1967) has suggested that it is more logical and convenient to express the reducing tendency of a redox system in terms of the activity of electrons. According to him, just as the proton activity, $-\log(H^+)$, is expressed as pH, the electron activity, $-\log e$, can be expressed as pE. In a redox reaction, $OX + ne = Red$, if the electron is handled as one of the reagents, the equilibrium constant (K) is

$$K = \frac{(Red)}{(Ox)(e)^n} \; .$$

Taking the logarithms and rearranging,

$$-\log (e) = \frac{1}{n} \log K + \frac{1}{n} \log \frac{(Ox)}{(Red)} \; .$$

If $-\log (e)$ is taken as pE and $\frac{1}{n} \log K$ is designated as pE°,

$$pE = pE^\circ + \frac{1}{n} \log \frac{(Ox)}{(Red)} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (13)$$

Equation (13) shows more obviously that the degree of oxidation in a system is negatively proportional to the activity of electrons. And this equation is simpler than equation (12) because the coefficient 0.059 is eliminated.

Whatever concept we may follow, from equations (12) and (13) it is found that the EMF or the electron activity of a system can be used as a qualitative and quantitative parameter. The terms E° or pE° being unique to each redox couple, if this value is known, the kind of redox couple operating in a certain system can be identified. If E° or pE° is known,

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the measured values of Eh or pE can be used to estimate the quantities of reduced or oxidized species in the system. So, the redox potential (Eh or pE) of the system is a very useful and important determination.

However, the correct interpretation of the measured redox potential is of utmost importance for the right use of this parameter. What should be born in mind is the fact that the measured values of Eh or pE are composed of two distinct terms: one E° or pE° and the other the ratio (Ox)/(Red). With the same falue of Eh or pE, if the E° or pE° are different, the value of (Ox)/(Red) will be different. Thus, the absolute value of Eh or pE by itself is not useful for the quantitative prediction of the activities of reagents involved in the system.

Attempts to correlate the redox potential with the concentration of certain components have not been successful when the Eh value alone is considered. Rich (1956) attempted to find a quantitative relationship between Eh values and the activity of Mn in soil systems without success. Copeland (1957) also failed in finding quantitative relationships between Eh values and the concentration of Mn and Fe in soil extracts.

Bohn (1968, 1969, 1971) considers that the measured EMF of soils are mixed potentials and, taking the aforementioned failures of Rich and Copeland as examples, discourages the quantitative use of Eh values.

On the contrary, Ponnamperuma and co-workers (1966) demonstrated the successful use of redox potential data in identifying the major redox couples in reduced soils. From the measurements of Eh, pH and the activities of Fe^{++}, they found that the systems $Fe(OH)_3$-Fe^{++}, $Fe_3(OH)_8$-Fe^{++} and $Fe(OH)_3$-$Fe_3(OH)_8$ operate in reduced soils.

Olomu, Racz and Cho (1973) observed that in soils saturated with water, incubated and showing Eh values of 255-470 mv, the system MnO_2-Mn^{++} operates as the major redox couple. Also they found that the Eh values did not show my (

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any connection with the activity of Fe^{++} in the studied systems.

These two findings are very suggestive, indicating that it is essential to identify the major redox couples operating in the system of interest before making quantitative interpretations of redox potential data in respect to the activities of a certain reagent in the system. The redox potential provides quantitative information on the activities of reductants or oxidants mainly for the major redox couples operating in the system.

As with attempts to correlate Eh values with the activity of Fe^{++} in systems where MnO_2-Mn^{++} operates as the major redox couple, the attempt to correlate Eh values with the activities of Mn^{++} in systems where Fe couples such as Fe_2O_3-Fe^{++} operate as major redox couples, may fail.

An example of the latter is found in the work of Ponnamperuma, Loy and Tianco (1968). With submerged soils, they failed in finding E° values identical to that for any theoretically known manganese system. The E° values calculated from measured Eh, pH and activities of Mn^{++} were always lower than the theoretical. Similar trends were experienced by Gotoh and Patrick (1972). These findings are indications that, in submerged (fully reduced) soils, manganese couples are not the major redox couples.

In summary, the redox potential of a soil is a useful parameter from which can be inferred not only the degree of oxidation or reduction, but also the quantitative and qualitative features of the agents involved in the redox reaction. But the full use of this parameter demands the knowledgeable interpretation of it.

(b) Problems Involved in the Measurement of Redox Potentials

Morris and Stumm (1967) discussed the conditions necessary for stable redox potential measurements. They pointed out that the low concentration of participating components, the absence of true equilibrium, and

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the irreversibility of electrode potentials make measurements of the redox potentials in natural systems quite unreliable and unquantitative from time to time. According to them for example, reliable potential measurements in Fe^{3+} -Fe^{++} systems require that the concentration of Fe^{3+} and Fe^{++} should exceed 10^{-5} mol/l. And they also pointed out that the systems $NO_3^- - NO_2^- - NH_4^+$, $SO_4^{--} - H_2S$, or CH_4 - Organic matter - CO_2, do not establish reversible electrode potentials.

Bohn (1968, 1969, 1971) maintained that redox potentials measured in soil systems are mixed potentials, thus they are not quantitative. He also discussed the difficulties in making reliable potential measurements in extremely diluted systems. Further, he pointed out that, in soil systems, the presence of hydrogen ions originating in non-redox reactions, makes the interpretation of measured redox potentials most difficult.

Apart from these theoretical problems in redox potential measurements, there are some technical difficulties too.

For the meaningful and successful measurement of redox potential, it is very important to have undisturbed and homogeneous samples. Many workers have measured the redox potential in situ. But, in reduced soils and muds, redox potentials vary widely from spot to spot (Jeffery, 1961; Aomine, 1962; IRRI, 1966; Yamane and Sato, 1970).

Aomine (1962) pointed out that in waterlogged paddy soils, reduction states are not even throughout the profile. He mentioned that this is especially true in highly productive soils. Workers at the International Rice Research Institute (IRRI,1966) found that, even in a greenhouse pot, potential readings taken from electrodes situated within one centimeter's distance of each other varied widely.

Ponnamperuma (1972a, b), in a review on the chemistry of waterlogged soils, has

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soils, has suggested that it would be more reasonable to measure redox potentials in the soil solution. He (1955) described a procedure for the collection of undisturbed soil solution samples. It seems likely that, by measuring redox potentials in soil solutions collected properly, the accuracy of the measurement could be improved remarkably. However, there arises one serious question; that is the explanation of the significantly large differences between the potentials measured in soils and those measured in soil solutions. Workers at IRRI (1966) reported that the Eh values of soils were lower than those of soil solutions by around 200 to 400 mv. Brooks et al. (1968), cited by Ponnamperuma (1972), observed that the potentials of marine mud cores were lower than those of their interstitial waters by about 200 mv. In Cho's work (1970) this difference was around 250 mv. Satisfactory explanations for these differences have not been given yet.

(c) Eh Values of Waterlogged Soils and Their Implications

Ponnamperuma (1965) has described the typical pattern of soil reductions: "Eh falls sharply upon flooding, reaches a minimum within a few days, rises rapidly to a maximum, and decreases asymptotically with time". Jeffery (1961), Yamane and Sato (1968) and Yamane (1969) expressed conformity with this remark. At the first minimum, Eh values are around -100 mv and, after the temporary maximum, they tend to stabilize at around -200 mv.

It is of special interest to find that, in spite of the fact that Eh values in soils fluctuate widely, the stabilized Eh values observed by many workers with a wide variety of soils fall in the vicinity of -200 mv consistently (Jeffery, 1961; Motomura et al., 1961; Motomura and Yamanaka, 1962; Ponnamperuma, 1965; IRRI, 1966; Yamane and Sato, 1968; Park et al., 1969; Cho, 1970; Park et al., 1971; Ayotade, 1972; Engler, 1972).

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Attempts to maintain the Eh value of submerged soils at elevated levels by incorporating highly oxidized substances have been made with different degrees of success (Aoki,1940; Mortimer,1941; Ponnamperuma,1955; Vamos,1958; Yamane,1958; Nhung and Ponnamperuma,1966; Yuan and Ponnamperuma, 1966; Engler,1972).

Theoretically, addition of such materials to soils as nitrate, manganese dioxide and other highly oxidized materials should maintain the redox potentials at higher levels. Some experimental results support this. Yamane (1958) could demonstrate that added nitrate tended to keep soil Eh at elevated values. Application of nitrate equivalent to 422 ppm of N kept the soil Eh at 200 mv for a prolonged time. But the application of nitrate at the rate of 258 ppm N did not show a prolonged effect, and addition of 35 ppm NO_3-N did not bring forth any effect. Nhung and Ponnamperuma (1966) showed that the application of MnO_2 at the rate of 1% of soil weight kept the Eh of an acid sulfate soil at 400 mv for 14 weeks; after this period, Eh tended to drop to the level of control plots. They also tested the effect of $Fe(OH)_3$. The application of $Fe(OH)_3$ at the rate of 0.5% of soil weight did not bring any changes in the redox potentials. Engler (1972) tested the effect of oxygen, potassium nitrate, manganese dioxide, ferricitrophosphate and ferric phosphate on the intensity of sulfur reduction in submerged soil. He observed that, except for oxygen, the application of these materials basically did not alter the degree of soil reduction. He could observe some effect, but it was slight and temporary. In his experiment, regardless of the treatments, the soil Eh values stabilized in the vicinity of -250 mv.

It is interesting to notice that the effects of application of highly oxidized materials on soil redox potentials are only short lived and that, upon the exp

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upon the expiring of the effects, Eh values drop down to the level of -200 mv.

An interesting question is, "What is the implication of the fact that, in most waterlogged paddy soils, Eh values stabilize at near -200 mv"? This question has not been raised frequently.

In exploring the answer to this question, Eh-pH diagrams depicting the stability areas for various forms of iron compounds are highly suggestive (Garrels and Christ, 1965; Ponnamperuma _et al._, 1967). According to these Eh-pH diagrams it seems likely that iron oxide -Fe^{++} couples would control the redox potentials in the majority of waterlogged paddy soils under fully reduced conditions.

On the other hand, the Eh values of soil solutions extracted from reduced paddy soils range from 200 to 0 mv (Ponnamperuma _et al._, 1965; IRRI, 1966; Cho, 1970; Ayotade, 1972; Lee, 1973). Ponnamperuma _et al_. (1967) calculated the E° values for reduced soil solutions from Eh, pH and activities of Fe^{++}. They evidenced that, in reduced soil solutions, the systems $Fe(OH)_3$ - Fe^{++}, $Fe_3(OH)_8$ - Fe^{++} and $Fe(OH)_3$ - $Fe_3(OH)_8$ operate. This means in other words, that iron hydroxide - Fe^{++} systems are the major systems controlling redox potentials in the interstitial solutions of reduced paddy soils.

According to Garrels and Christ (1965), in the systems Fe_2O_3 - Fe^{++} and Fe_3O_4 - Fe^{++}, Eh, pH, and the activities of Fe^{++} have the following relationships:

$$Eh = 0.728 - 0.059 \log Fe^{++} - 0.177 \text{ pH} \quad \ldots\ldots\ldots\ldots (14)$$

$$Eh = 0.980 - 0.0885 \log Fe^{++} - 0.236 \text{ pH} \quad \ldots\ldots\ldots\ldots (15)$$

Ponnamperuma _et al_. (1965) presented the following equations for $Fe(OH)_3$ - Fe^{++} and $Fe_3(OH)_8$ - Fe^{++} systems.

$$Eh = 1.058 - 0.059 \log Fe^{++} - 0.177 \text{ pH} \quad \ldots\ldots\ldots\ldots (16)$$

$$Eh = 1.373 - 0.885 \log Fe^{++} - 0.236 \text{ pH} \quad \ldots\ldots\ldots\ldots (17)$$

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It is very interesting to observe the relatively high conformity between the practically measured values of the activity of Fe^{++} in reduced soils and those predicted by theoretical equations. When the commonly observed values of Eh ($\hat{=}$ - 250 mv) and pH ($\hat{=}$ 6.5) in soil systems are put into the equations (14) and (15), the activities of Fe^{++} are found to be $10^{-2.9}$ and $10^{-3.4}$ mol/l, respectively. These values, in fact, are close to the activities of Fe^{++} of reduced soils. Similarly, by putting the commonly observed Eh and pH values in equations (16) and (17), the activities of Fe^{++} are found to be $10^{-2.9}$ and $10^{-3.3}$ mol/l, respectively. These are close to the commonly encountered values in reduced soil solutions.

These facts obviously suggest that, in reduced soils systems, the redox potentials are controlled by iron oxide - Fe^{++} couples and that, in soil solutions separated from reduced soils, the iron hydroxide - Fe^{++} systems control the redox potentials.

It has been reported that the differences between the Eh values of soil systems and those of soil solution range from 250 to 350 mv (IRRI,1966; Cho,1970; Lee and Hong,1974), with an average difference of 300 mv. The fact that the magnitude of this difference coincides roughly with the difference in E° values of the redox couples of Fe_2O_3 - Fe^{++} and that of $Fe(OH)_3$ - Fe^{++} is another suggestion that soil is an iron oxide - Fe^{++} system and the soil solution is an iron hydroxide - Fe^{++} system.

2. pH of Waterlogged Soils

Changes in pH always accompany the reduction of soils. Sometimes pH goes up and sometimes it drops. Ponnamperuma (1972a) describes this feature thus: "The overall effect of submergence is to increase the pH of acid soil and to depress the pH of sodic and calcareous soils. Thus submergence makes the pH values of acid soils (except those low in iron) and alkaline soils

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converge to pH 7.0". Many experimental findings support this view (Jeffery, 1961; Motomura *et al.*,1961; Ponnamperuma,1965; IRRI,1966; Yamane and Sato, 1968; Park *et al.*,1969; Cho,1970; Park *et al.*,1971; Ayotade,1972; Cho *et al.*, 1972).

(a) Factors Affecting the pH of Reduced Soils

As early as 1920, Gillespie noticed the decrease in soil acidity upon the reduction of soil. Subrahmanyan (1927) attributed the increase of pH in reduced soils to the occurrence of ammonia. Schollenberger (1928) demonstrated that the increase of alkalinity during the course of soil reduction was due to the reduction of manganic oxides. He could observe the parallelism between the increase of soil alkalinity and the manganous manganese produced. Joffe (1935) connected the increase of pH by the reduction of soils with the reduction of iron oxide by stating, "In the reduction process, the ferric iron gives rise to ferrous iron, and in the case of the hydroxide the weak bases change into the stronger ferrous iron bases. Partly because of this fact, therefore, one should expect a higher pH in the gley horizon".

As already mentioned, the anaerobiosis taking place in submerged soils results in the occurrence of materials both acidic and alkaline. Such substances as CO_2, organic acids, and H_2S are acidic, while ammonia, ferrous iron hydroxide, and manganous hydroxide are alkaline. Thus the pH changes upon the submergence of soil will be decided by the quantities of acidic substances and alkaline substances produced and by their chemical characteristics. From this view, it is noteworthy to consider the quantitative aspects of the substances produced via anaerobiosis in submerged soils.

Firstly, acidic substances will be considered. Organic acids, CO_2 and H_2S are acidic products. Among these, CO_2 seems to be most influential on

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the soil reaction, because the quantity of CO_2 exceeds the others overwhelmingly. According to Yamane and Sato (1961b), in an alluvial soil, CO_2 produced at the peak was 250 ml/100g. Ponnamperuma (1972a), citing a report of IRRI (1964) says that one to three tons of CO_2 are produced in the plowed layer of 1 hectare of a soil during the first few weeks of submergence. If three tons of CO_2 in plow layer soil from 1 ha is converted into milliequivalents per 100g, it is roughly 14 me/100g. Apart from the quantity (capacity term) of CO_2, the intensity of CO_2, that is the partial pressure of CO_2, is also remarkable, with an average value of around 0.2 atm in fully reduced soils (Bell,1969; Cho, 1970; Ayotade,1972).

As to the alkaline substances, ammonia, although it is a relatively active alkali, being small in quantity, its contribution to the increase of pH in submerged soils cannot be too great. Reported figures for ammonia in fully reduced soils are less than 100 ppm, which is less than 1 me/100g (Ponnamperuma,1965; Cho,1970; Cho and Chung,1971). Higher concentrations may be found in soils very high in organic matter.

The reduction of oxides of manganese certainly would result in increase of pH. The following reactions show this clearly:

$$MnO_2 + 2H_2O + 2e \dashrightarrow Mn^{++} + 4OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

$$Mn_2O_3 + 3H_2O + 2e \dashrightarrow 2Mn^{++} + 6OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

$$Mn_3O_4 + 4H_2O + 2e \dashrightarrow 3Mn^{++} + 8OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

According to Bostroem (1967), in redox reactions when the ratio (R) OH^-/e is greater than 1.0, the reductive reaction would yield an increase in alkalinity. In the reactions (18),(19) and (20), the values of "R" are always greater than 1.0. Thus the reduction of manganese would certainly result in the elevation of soil pH, if the pH of the soil was not high before the reduction. But here again, a quantity term should come into the consideration.

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The amounts of reducible manganese in ordinary paddy soils are less than those of active iron (Ponnamperuma, 1965; Hong, 1972).

Reduction of iron oxides results in increased alkalinity, as with manganese oxides:

$Fe_2O_3 + 3H_2O + 2e = 2Fe^{++} + 6OH^-$ . . . . (21)

$Fe_3O_4 + 4H_2O + 2e = 3Fe^{++} + 8OH^-$ . . . . (22)

Summarized world wide figures for the contents of active iron in paddy soils have not been reported. However, from several sources (Ponnamperuma et al. 1967, Ponnamperuma 1965, Park 1966, Cho 1970, Ayotade 1972, Hong 1972) it can be estimated that the active Fe contents range from 0.2 to 3.0% with an average of around 1.0% or a little higher. When 1.0% of Fe as Fe_2O_3 is reduced to Fe_3O_4, it is roughly estimated that around 12 me/100g of hydroxyl ion would be produced.

Consideration of the quantitative aspects of substances produced in the course of soil reaction leads to the conclusion that the alkalinity developing from the reduction of iron oxide and the acidity due to CO_2 are the major factors that determine the pH values of submerged ferruginous soils. The pH of reduced paddy soils normally falls in the range from 6.0 - 7.0, and this may be the equilibrium pH of systems such as $Fe_2O_3 - FeCO_3 - H_2O - CO_2$ or $Fe_3O_4 - FeCO_3 - H_2O - CO_2$.

Ponnamperuma, Martinez and Loy (1965) proposed that the pH of reduced ferruginous soil seems to be determined by the system $Fe_3(OH)_8 - H_2O - CO_2$ and that, in calcareous and sodic soils, pH is determined by the respective systems $CaCO_3 - H_2O - CO_2$ and $Na_2CO_3 - H_2O - CO_2$.

(b) Relationships Between the Redox Potential and pH.

The activity of hydrogen ion directly and indirectly influences the Eh or pE values. Reduction of O_2 to H_2O in the presence of H^+ is an example of the hyd

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of the hydrogen ion directly influencing the Eh or pE:

$O_2 + 4H^+ + 4e = 2H_2O$ . . . . (23)

$Eh = 1.229 + 0.015 \log O_2 - 0.059\ pH$ . . . . (24)

or $pE = 20.80 + 0.25 \log O_2 - pH$.

It is seen that in the $O_2 - H_2O$ system, the slope Eh/pH being -0.059, a change of one pH unit will result in a change of 0.059V, or 59 mv.

When the solubility of oxidant or reductant is controlled by the pH of the system, the hydrogen ion influences the redox potential indirectly. For instance, in a highly acidic system, reduction of ferric iron to ferrous iron does not involve any connection with pH:

$Fe^{+++} + e^- = Fe^{++}$ . . . .(25)

$Eh = 0.771 + 0.059 \log \frac{(Fe^{+++})}{(Fe^{++})}$ . . . .(26)

At intermediate pH ranges, where the ferric iron exists as $Fe(OH)_3$ and the ferrous iron as Fe^{++}, the reduction of Fe is,

$Fe(OH)_3 + 3H^+ + e = Fe^{++} + 3H_2O$

For this case, Eh is:

$Eh = 1.058 - 0.059 \log Fe^{++} - 0.177\ pH$ . . . . (27)

And, in the alkaline condition, where both ferric iron and ferrous iron exist in hydroxide form, the reduction of Fe is written as:

$Fe(OH)_3 + H^+ + e = Fe(OH)_2 + H_2O$

For this,

$Eh = 0.273 - 0.059\ pH$ . . . .(28)

It is remarkable to notice that there is a wide variation in the slope of Eh/pH among the redox couples of Fe. In the strongly acidic condition it is 0; at intermediate pH, - 175 mv/pH; and in alkaline condition, - 59 mv/pH. A similar principle applies to manganese systems, too. These suggest that in reduced soils the slope Eh/pH would vary widely depending on the kinds of major redc

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However, in spite of this, as Ponnamperuma (1972a) pointed out, many scientists have been using the theoretical coefficient of the O_2 - H_2O system, that is - 60 mv/pH, in correcting the Eh values measured at different pH's to that at a certain pH (as Eh6 or Eh7). It is not logical to correct the Eh values using -60 mv/pH as the correction factor, disregarding the characteristics of the system. Various values for the correction coefficient have been reported. Ponnamperuma (1955) reviewing this subject cited values ranging from -27 to -100 mv/pH (Willis,1932; Puri and Sarup,1938; Buehrer et al.,1939). Patrick (1960) gives the highest value of -232 mv/pH. Workers at the IRRI (1964) reported -56 mv/pH for oxidized soils and -30 to -120 mv/pH for reduced soils.

Kohnke (1934) clearly demonstrated the Eh-pH relationships in the Fe^{+++} -- Fe^{++} systems. He found the coefficient to be -174 mv/pH, through titration with NaOH of solutions containing equal amounts of Fe^{+++} and Fe^{++}. He also found that the addition of such substances as oxalate, citrate and certain clay minerals to the Fe-containing solution altered the Eh-pH relationships significantly, and attributed this to the effect of formation of Fe complexes.

Jeffery (1961) speculated that, in waterlogged paddy soils, the major redox couple would be $Fe(OH)_3$ - Fe^{++}; thus Eh of the system could be expressed as $Eh = 1.033 - 0.059 \log Fe^{++} - 0.180$ pH. On the basis of this consideration he suggested that the term γEh (= Eh + 0.18 pH) would be a more meaningful criterion than the absolute value of Eh in identifying the oxidation-reduction status of a soil. This suggestion, however, could not meet wide acceptance, because the significance of the term γEh is not justified, and at the same time, it is not always true that $Fe(OH)_3$ - Fe^{++}

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It seems that earlier workers have been missing some serious logical points in studying the Eh-pH relationships in reduced soil systems. They usually measured the Eh and pH of soils at certain time intervals. From these observations, the Eh-pH relationships were found. Eh-pH relationships found in this way cannot be meaningful because, with time of submergence, not only do Eh and pH change, but also the nature of the dominant redox couple. For example, with iron oxide systems it is expected from the stability diagrams for different iron oxides (Garrels and Christ,1965) that, at the earlier reduction stages, the major redox couple would be Fe_2O_3 - Fe^{++} and, later, Fe_3O_4 - Fe^{++}. If this is the case, since each system has different E° values and Eh-pH relationships, the measurement of Eh and pH at different times will not reflect the Eh-pH relationship of any particular redox couple.

In practical soils, if the major redox systems operating in them are not known, the conversion of the Eh measured at different pHs' to that at a certain pH is impossible and it is meaningless to use the conventional conversion factor of -60 mv/pH. From a different point of view, Ponnamperuma (1972a) criticizes the conversion of Eh to Eh6 or Eh7 by stating, "For most mineral muds, adjustment of Eh for pH is an unnecessary refinement because the pH values of reduced muds are about 7 and mud potentials are in any case imprecise".

3. Soil Gases

Change in the composition of soil gases is also one of the phenomenal features of submerged soils. Their influences on the chemistry of submerged soils cannot be overemphasized.

(a) Accumulation of CO_2

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disappeared in a day, CO_2 evolution initiated within a week and, at the end of the second week, accumulation of Ch_4 set forth. They found that after 20 days of submergence, CO_2 comprised around 75% of soil gas by volume. Significant accumulation of CO_2 in submerged soils has been observed by many workers (Yamane and Sato, 1961b; IRRI, 1964; Bell, 1969; Cho, 1970; Ayotade, 1972; Cho et al., 1972). From the reported information, it is found that CO_2, like the other soil reduction products, attains its peak within a few week's submergence at a partial pressure as high as 0.5 - 0.9 atm and, after the peak, drops quickly to be stabilized at a level of 0.1 - 0.3 atm thereafter.

(b) Significance of CO_2 Accumulation

The carbon dioxide dissolves in water, forming carbonic acid. Carbonic acid dissolves sparingly soluble salts and, at the same time, it precipitates metallic ions forming carbonates. Because of this delicate behavior of CO_2 in chemical reactions, many intensive studies have been made on the systems M_2SO_3-H_2O-CO_2 and MCO_3-H_2O-CO_2.

Frear and Johnston (1929) presented data showing the increased solubility of calcite under elevated partial pressure of CO_2. Bradfield (1941) observed similar aspects. Langelier (1936) derived an equation which defines the pH in the system $CaCO_3$-H_2O-CO_2 as follows:

$$pHc = (pK_2 - pK_s) + pCa^{++} + pAlK \quad \ldots\ldots\ldots\ldots \quad (29)$$

where, pHc = theoretical pH, K_2= second dissociation constant of H_2CO_3, K_2 = solubility product of $CaCO_3$, and AlK = titratable base.

Later, Simmons (1939) suggested a more refined pH equation for the same system:

$$pH = pK_1 - 0.5\,\mu - pHCO_3 + pH_2CO_3 \quad \ldots\ldots\ldots\ldots \quad (30)$$

where, K_1 = first dissociation constant of H_2CO_3, μ = ionic strength.

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Whitney and Gardner (1943) attested this equation. Cole (1957) used another form of equation defining the relationships among pH, activity of Ca^{++} and the partial pressure of CO_2:

$$pH - 1/2\ pCa^{++} = 4.85 - 1/2 \log PCO_2 \ldots\ldots\ldots\ldots (31)$$

where PCO_2 denotes the partial pressure of CO_2.

The usefulness of this equation has been proven by Olsen and Watanabe (1959) and Clark (1964). They used the term pH - 1/2 pCa^{++} as the criterion for identifying the presence of $CaCO_3$-H_2O-CO_2 systems in calcareous soils.

In waterlogged soils, the partial pressure of CO_2 has been known to influence the pH, the activities of metallic ions and Eh-pH relationships (IRRI,1964, 1966; Ponnamperuma et al.,1965; Ponnamperuma,1966; Kyuma and Kawakuchi,1966; Kyuma,1967; Ponnamperuma et al.,1969).

Ponnamperuma, Martinez and Loy (1965) discussed the theoretical relationships among the activities of metallic ions, pH, redox potential and the partial pressure of CO_2 for various carbonates. They also found that the pH of submerged soils was highly correlated with the partial pressure of CO_2. Ponnamperuma (1966) presented some theoretical equations on the relationships among pH, hydroxide potentials, the activities of metallic ions and the partial pressure of CO_2. His equations are more refined compared to previously reported ones. Generalized equations for pH and hydroxide potentials in $MCO_3 - H_2O - CO_2$ systems are:

$$pH = 1/3 (\log 2 + pK_2 - pK_s) + 2/3 (pK + pK_1 - \log PCO_2)$$
$$+ 1/3 (\log \gamma HCO_3^- - \log \gamma M^{++}) \ldots\ldots\ldots\ldots (32)$$

and

$$pH - 1/2\ pM^{++} = 1/2 (pK + pK_1 + pK_2 - pK_s) -$$
$$1/2 \log PCO_2 \ldots\ldots\ldots\ldots\ldots\ldots (33)$$

where, K, K_1, K_2, K_s are the dissolution constant of CO_2, first and second dissociation constants of H_2CO_3 and the solubility product of MCO_3,

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respectively. γHCO_3^- and γM^{++} are the activity coefficients for HCO_3^- and M^{++}.

Kyuma and Kawaguchi (1966) and Kyuma (1967), discussing the Eh-pH relationships in reduced soils, pointed out that the presence of CO_2 at the levels observed in ordinary paddy soils should be taken into consideration in the derivation of theoretical equations for Eh-pH relationships. Ponnamperuma, Castro and Valencia (1969) experimentally demonstrated the validity of previously derived theoretical equations on the influence of CO_2 on pH in various carbonate systems. They also showed that, in reduced soils, the pH of the soil was very sensitive to the partial pressure of CO_2. With different soils, they found that pH was highly correlated with PCO_2 as:

$$pH = 6.1 - 0.67 \log PCO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (34)$$

The presence of CO_2 in reduced soils not only influences the pH of the system; its influence on the activities of metallic ions is expected to be significant. It is predicted from the solubility products of various metallic carbonates (Latimer 1961) that iron carbonate (siderite)is one of the most stable carbonates in reduced soils.

The precipitation of Fe^{++} by carbonate in reduced soils seems to be a remarkable feature to be studied further. If the concentration of Fe^{++} in reduced soils is controlled by the solubility of the ferrosoferric hydroxide (Ponnamperuma, 1965; Ponnamperuma _et_ _al_., 1967), its concentration would be approximately 300 ppm at pH 6.5 and 3000 ppm at pH 6.0. These concentrations of Fe^{++} may be too high for the successful performance of rice plants. Carbonate ions by complexing with sulfide ion in precipitating the Fe^{++} ion, allows the sulfide to remain as free H_2S to a certain extent (Tanaka _et_ _al_., 1968). It has also been pointed out that the formation of vivianite

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($Fe_3(PO_4)_2$) is influenced by the presence of carbonate in reduced soils (Rosenquist, 1970).

C. Chemistry of Sulfur in Submerged Soils

Sulfur is one of the more abundant and reactive elements in nature. Its chemistry is known to be complex and to have significant impacts on both natural and biological processes. Its diversified chemical characteristics are well reflected in the electronic configuration of the element; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$. The element, by yielding six electrons (3s and 3p), attains the stable electronic configuration of neon and, by accepting two electrons to fill the unfilled 3p, it attains another stable electronic configuration, that of argon. Thus, +6 is the highest and most stable oxidation state in oxidized environments, while -2 is the lowest and stable under reduced conditions. However, depending upon the redox status of the reaction media, the element attains the oxidation states of +5, +4, +3, +2.5, +2 and 0, as well (Latimer,1961).

1. Biochemical Transformation of Sulfur in Submerged Soils

Submerged soil is a typical example of a reduced biological environment. Accordingly, the transformations of S in this system are inclined toward its reduction, and the reduction is mediated by biological processes. Release of reduced sulfur during putrefaction of proteins is also a significant feature of S transformation (Alexander, 1961; Freney, 1967).

Reduction of inorganic S is mediated by specific microorganisms (Starky,1950; Postgate, 1959; Alexander, 1961), while putrefaction is by nonspecific organisms (Alexander ,1961). Reduction of inorganic S, mainly sulfate, is carried out by two distinct mechanisms; one is biosynthetic reduction and the other is metafermentation (Alexander,1961; Freney,1967). As seen in following schemes, the former does not result in the accumulation of sulfide

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of sulfide in the soil, while the latter does (Freney 1967).

Biosynthetic reduction of sulfate:

$$\begin{tikzcd}
SO_4 \arrow[r] & APS \arrow[r] & PAPS \arrow[r] & SO^{--} \arrow[r] \arrow[d] & S^{--} \arrow[r] & \text{Cysteine} \\
 & & & S_2O_3^{--} \arrow[ur] & &
\end{tikzcd}$$

where, APS = adenosine phosphosulfate, PAPS = phosphoadenosine phosphosulfate.

Metafermentation:

$$CH_3CHOHCOOH + H_2SO_4 \longrightarrow 2CH_3COOH + 2CO_2 + H_2S + 2H_2O.$$

Among the multitude of S transformations, the one that has more significant impacts on the chemistry of submerged soils than any other, is the metafermentative reduction of sulfate. Genus Desulfovibrio is known to contain the dominant species responsible for the reduction of sulfate and other forms of inorganic S (Alexander, 1961; Starkey, 1966).

Reduction of sulfate is affected by many factors. Starkey and Wight (1945) suggested that the optimal pH would be 7.0. Connel and Patrick (1969) reported the pH range for sulfate reduction to be between 6.0 and 9.5. Sulfur-reducing bacteria being strictly anaerobic, the active biological reduction of sulfate has been known to be sensitive to the electron activity or redox potential of soils. Various Eh values have been reported for the initiation of sulfate reduction.

Akabori and Tamia (1950) mentioned the redox potential values of -175 to -283 mv for the accumulation of H_2S. Such values as -50 mv (Suzuki and Honya, 1950), -150 mv (Takai et al., 1957; Patrick and Mahapatra, 1968; Connel and Patrick, 1969), -180 mv (Baas-Becking et al., 1960), and +100 mv

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Although the reported Eh values vary widely, it seems that the reduction of sulfate will be active at Eh values of -150 mv or lower. Theoretical considerations also support this. The reduction of sulfate to sulfide can be expressed by the following scheme (Morris and Stumm, 1967; Ponnamperuma, 1972b):

$$1/8\ SO_4^{--} + 5/4H^+ + e = 1/8\ H_2S + 1/2\ H_2O \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (35)$$

and $pE = 5.12 - 1/8(pSO_4^{--} - pH_2S) - 5/4\ pH$

If the commonly observed pH value 6.5 is substituted,

$$pE = -3.00 - 1/8\ (pSO_4^{--} - pH_2S)$$

$$\text{or, } -1/8(pSO_4^{--} - pH_2S) = pE + 3.00$$

Under the condition in which the activities of SO_4^{--} and H_2S become equal, as the result of reduction of sulfate, pE + 3.00 = 0, or pE = -3.00. This means that where there is active reduction of sulfate, pE = -3.00. The value of -3.00 in pE is -177 mv in Eh units which is fairly close to frequently reported values for sulfate reduction.

The contribution of putrefaction to the accumulation of sulfide in submerged soils has been usually disregarded (Starkey and Wight, 1945; Postgate, 1959). However, if H_2S at very low concentration is assumed to be influential on the rice plant, the production of H_2S by putrefaction of protein should be considered as a matter of great significance. Ayotade's (1972) data on the dynamics of H_2S in reduced soil solutions reflects this situation convincingly. His data shows that the activity of H_2S attains its maximum at three week's submergence and before the disappearance of sulfate. Engler (1972) also experimentally showed the mineralization of organic S as sulfide in waterlogged soil.

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during putrefaction, several other transformations of S occur in waterlogged paddy soils. In the presence of light, photosynthetic oxidation of sulfide is mediated by such organisms as Thiorhodaceae and Chlorobacteriaceae (Delwiche, 1967). This process is expressed as:

$$H_2S + 2H_2O + 2CO_2 \xrightarrow{h\lambda} 2(HCHO) + H_2SO_4 \ldots\ldots\ldots\ldots \quad (36)$$

However, the significance of this process in the chemistry of flooded soils has not been properly estimated yet.

It is also known that oxidation of sulfide can occur in soil intimately in contact with rice roots in waterlogged paddy fields. Pitts _et_ _al_. (1972a) reported that they could isolate _Beggiatoa_ from rice rhizosphere in a Louisiana soil. This organism is capable of oxidizing sulfide to elemental sulfur intracellularly. Han (1973) reported he could isolate some Bacillus-like organisms from the rice rhizosphere in submerged soil.

2. Forms of Sulfide in Reduced Soils

In the absence of metallic ions, sulfide in aqueous solution exists as H_2S, HS^- and $S^{=}$, depending upon the pH of the solution. In some specific situations, the occurrence of persulfide (S_2^{--} as H_2S_2) and polysulfides (S_3^{--}, S_4^{--} . . . . . S_n^{--}) is also possible (Moeller 1963).

In contact with metallic ions, sulfide combines with them to form the sparingly soluble metal sulfides. From the solubility products, it is expected that, in reduced soils, FeS, MnS, ZnS, and CuS can occur.

However, when the total amounts and the activities of metals which might be present are considered, ferrous iron seems to be the one most likely to control the activity of sulfide. Manganese sulfide may influence the activity of sulfide in some soils high in reducible Mn, but in reduced ferruginous soils its occurrence is doubtful (Ayotade 1972). The higher solubility of MnS (7×10^{-16}) than of FeS (4×10^{-18}) (Latimer 1961) and the lower concentration of Mn^{++} (10^{-3} to 10^{-4} M) than of Fe^{++} (approximately 10^{-3} M) in solutions from reduced soils (Ponnamperuma, 1955; Cho, 1970; Ayotade, 1972) may not allow the formation of MnS.

The occurrence of ZnS in reduced soils has been shown (Katyal, 1972; Ayotade, 1972). However, its quantity being low in soils, Zn cannot be the factor that controls the activity of sulfide.

Ayotade (1972) and workers at IRRI (1973) proved the occurrence of FeS in reduced paddy soils by showing the constancy of the function $pFe^{++} + pS^{--}$ at approximately 18.4 which is the criterion for the presence of FeS.

The term iron sulfide is a collective term. According to Berner's (1964) review, iron sulfide includes a variety of compounds: troilite (FeS), hydrotroilite ($FeS \cdot nH_2O$), pyrrhotite (FeS), kansite (FeS), marcasite (FeS_2), pyrite (FeS_2), melnikovite (FeS_2), etc. It was pointed out that the formation of the various sulfides is influenced by such factors as pH, temperature, the presence of oxidizing agents, and the characteristics of Fe compounds. He showed that, under low temperature and slightly acidic to alkaline conditions, the formation of tetragonal or amorphous FeS is favored over other forms of iron sulfide.

In studying the activity relations of H_2S and Fe^{++} in reduced soils, FeS has been taken as the compound that controls the activity of sulfide in solution (Ponnamperuma, 1955; Park, 1966; Ayotade, 1972).

However, recently Pitts (1971) suggested that the relationships among pH and the activities of Fe^{++} and H_2S in the reduced soils should be sought on the basis of the following reaction:

$$2Fe^{++} + H_2S + HS^- + S^= = FeS + FeS_2 + 3H^+ + 2e \; . \; . \; . \; . \; . \; . \; (38)$$

Further, Pitts (1971) and Pitts, Allam and Hollis (1972b) maintained that, in the ranges of Eh and pH observed in reduced paddy soils, the stable iron sulfide is

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sulfide is FeS_2. From this consideration they tried to define the Eh-pH-Fe^{++}-H_2S relationships from the redox reaction:

$$Fe^{++} + 2H_2S = FeS_2 + 4H^+ + 2e \quad \ldots \ldots \ldots \ldots \quad (39)$$

The validity of considering FeS_2 to be the factor that controls the activities of H_2S and Fe^{++} in normal paddy soils seems doubtful. In soils kept under temporary submergence, as in the case of paddy soils, iron sulfide is FeS, black in color. Pyrite is formed by the aging of FeS under prolonged submergence of soils (Ponnamperuma, 1972a). Berner (1964) reported that unusual conditions were necessary for the synthesis of FeS_2; the reaction of H_2S with $FeSO_4$ or Mohr's salt at pH of 3 yielded FeS_2; at pH values of 7 and 9, the same reaction resulted in amorphous or tetragonal FeS. More detailed discussion on this point will be given in the following chapter.

D. Chemistry of Iron in Submerged Soils

Iron is one of the most abundant elements in natural systems (Krauskopf, 1967). Having the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$, Fe is actively involved in oxidation-reduction and complexation reactions. Oxidation states of Fe° and F^{+6} together with the commonly observed Fe^{++} and Fe^{3+} are known. But in natural soil and water systems, Fe^{++} and Fe^{3+} are most important (Garrels and Christ, 1955). The ions Fe^{++} and Fe^{3+} exist as hexaquocomplex ions, with the hybridized electronic configuration sp^3d^2. Such ions as CN^- form very stable complexes with Fe^{++} and Fe^{3+}, in which the hybridized electronic configuration is d^2sp^2 (Keller and Parry, 1956; Martell and Calvin, 1962). The electronic configuration d^2sp^2 is very important for the chemistry of Fe because the chelation of Fe is possible due to this electronic arrangement (Wallace, 1962).

The transformations of Fe in nature are very sensitive to the oxidation-reduction status and the pH of the system (Latimer, 1961; Garrel and Christ, 1965; Ponnamperuma,1972b). Thus, in systems where there are changes in redox status and in acidity, such as in submerged soils, Fe plays a very important role.

1. Chemical Transformation of Iron in Submerged Soils

Oades (1963) reviewed extensively the literature on forms of Fe in soils, especially on ferric iron oxides. In oxidized soils, hematite, maghemite, goethite, lepidocrocite, and hydrated ferric hydroxide are the major Fe compounds. In gleyed soil, lepidocrocite seems to be ubiquitous (Brown, 1953, 1954; Kamoshita and Iwasa,1959; Kataoka and Kitamura,1959; Kojima and Kawaguchi,1968; Asami,1970). Brown (1954) reported that lepidocrocite was observed in the brown orange mottles of all soils studied, while goethite was found in some soils. Kamoshita and Iwasa (1959) confirmed this. Kojima and Kawaguchi (1968) in a study of Fe mottles in paddy soils, found that the mottles consisted of lepidocrocite in the majority of cases.

Asami (1970) investigated the degree of reducibility of different forms of ferric iron oxide. He found that the ease of reduction increased in the order goethite > hematite > γ -FeOOH > lepidocrocite.

The mechanisms of Fe reduction in gley soils have been recently reviewed by Aristovskaya and Zavarzin (1971). Starkey and Halvorson (1927) observed the reduction of ferric iron in anaerobic cultures of microorganisms. They emphasized the importance of lowered redox potential in anaerobic microbial systems in connection with the dissolution of Fe. Halvorson (1931) again pointed out that, in anaerobic microbial systems, ferric iron will be reduced since oxygen tension is low. Roberts (1947) identified _Bacillus polymixa_ as an organism that can reduce the ferric iron to ferrous iron metabolically. Bromfield (1954) pointed out that _B_. _circulans_ also is capable of reducing ferric iron. Motomura _el_ _al_. (1961) observed the parallelism

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Thus, it appears that the reduction of ferric iron is mostly due to the activities of anaerobic microorganisms. Although the involvements of microorganisms in the reduction of ferric iron in soils has been verified, the biochemical mechanisms have not been fully elucidated. Kamura and Takai (1961) maintained that there are two distinct mechanisms for Fe reduction; one is metabolic reduction and the other is indirect reduction. In the former case, ferric iron oxide plays the role of electron acceptor for the metafermentative oxidation of organic substrates, and, in the latter, ferric iron is reduced by certain microbial metabolites. Direct information on which mechanism is more prevalent in natural soils is scarce. Aristovskaya and Zavarzin (1971) seemingly put more emphasis on the latter. If the reduction of Fe is assumed to occur through reaction with microbial metabolites, the oxidation-reduction of Fe in reduced soils can be taken as a reversible chemical process since oxidation is spontaneous under aerobic conditions.

2. Forms of Iron in Submerged Paddy Soils

Ponnamperuma (1972a) has discussed this subject. He records such compounds as hydrated magnetite ($Fe_3O_4 \cdot nH_2O$ or $Fe_3(OH)_8$) and hydrotroilite ($FeS.nH_2O$) as the most probable Fe compounds to occur in temporarily reduced soils. He pointed out that, if the reduced condition is prolonged, these compounds may age, resulting in magnetite and pyrite. He also pointed out that such compounds as siderite, greenalite ($FeSiO_3$), chamosite ($FeSiO_3$), and vivianite ($Fe_3(PO_4)_2.8H_2O$) may occur in soils kept under reduced conditions for a long period of time.

For understanding the role of Fe in the chemistry of reduced soils, it is of utmost importance to identify the Fe compounds which control its ionic equilibria. Ponnamperuma with his co-workers (1966) considered that the bulk of ferrous iron in reduced soils, other than acid sulfate soils, exists as ferrosoferric hydroxide ($Fe_3(OH)_8$), which was described by Arden (1950). Ponnamperuma (1965) and Ponnamperuma et al. (1967) surmised that $Fe3(OH)_8$ would control the concentration of ferrous iron in reduced soils. Upon this assumption, Ponnamperuma (1965, 1972a, b) considers that the activity of ferrous iron in solution in fully reduced soils can be predicted by following equation:

$$pFe^{++} = 2pH - 10.4 \quad \text{. . . . . (40)}$$

In theoretical studies with carbonate systems, Ponnamperuma (1966) derived an equation for pH-PCO_2 relationships in the $Fe3(OH)8$-CO_2 system as follows:

$$pH = 6.19 - 1/3 \log PCO_2 + 1/3(\log\gamma HCO_3^- - \log\gamma Fe^{++}) \quad \text{. . . . . (41)}$$

where $PCO2$ is the partial pressure of CO_2, γHCO_3^- and γFe^{++} are the activity coefficients of HCO_3^- and Fe^{++}, respectively.

He considered that, since both $Fe_3(OH)_8$ and $CO2$ exist simultaneously in reduced soils, the above equation can be used for the prediction of pH from PCO_2 or vice versa.

Ponnamperuma, Castro and Valencia (1968) tested the validity of this equation with soil and with pure $Fe_3(OH)_8$ systems. They found that, in both soil and pure $Fe_3(OH)_8$ systems, there were highly significant correlations between pH and the partial pressure of CO_2, but the coefficient for log PCO_2 was always greater than that of the theoretical equation. The empirically obtained pH-PCO_2 equation was:

$$pH = 6.1 - 0.58 \log PCO_2 \quad \text{. . . . . (42)}$$

When equations (41) and (42) are compared, it is found that, in the empirical equation, the coefficient for log PCO_2 is much greater than that of the theoretical equation. Ponnamperuma and co-workers (1968) did not give a detailed explanation for this. In fact the empirically observed coefficient for log PCO_2 is close to that in the theoretical equation for MCO_3-H_2O-CO_2 (where M is the metal ion) systems, indicating the possibility that the $FeCO_3$-H_2O-CO_2 system was present in the reduced soils.

Although there is the consideration that the concentrations of Fe^{++} observed in the reduced soil solutions are too high to be accepted as the concentration of Fe^{++} in equilibrium with $FeCO_3$ in the solution phase (Ponnamperuma,1972a), the involvement of the $FeCO_3$-H_2O-CO_2 system in reduced soils seems to be a matter of high possibility.

Hem (1960a, b) speculated that the activity of Fe^{++} in the waters of reduced environments may be influenced by $FeCO_3$ system. Garrels and Christ (1965, p.208-210) and Bostroem (1967, p.307) in diagrams for this stability fields of Fe compounds showed that, in the ranges of Eh and pH encountered in ordinary reduced soils, $FeCO_3$ is the stable Fe compound. Yamane (1970) also showed a similar picture.

3. Factors Determining the Activity of Iron in Reduced Soils.

From the foregoing discussion, it is clear that the concentration of Fe in reduced soil solutions are definitely influenced by Eh, pH, the partial pressure of CO_2 and the solubility characteristics of Fe compounds which are in equilibrium with the dissolved Fe.

In addition to these, it is known that there are other factors that influence the concentration of Fe in soil solution. They include the presence of Fe chelates and the ion-pairs of Fe compounds.

Recently Park (1971) reviewed the work on natural chelates in soils. Jones and Wilcox (1929) noticed the effect of organic acids, produced in the course of decomposition of organic matter in soil, on the movement of Fe through the soil profile. Bremner _et al_. (1946) surmised that part of the polyvalent metals in soil are combined with organic compounds as coordination complexes. Bloomfield (1953a, b) observed that certain organic compounds in scots pine needles and in leaves of kauri can mobilize Fe and Al in the soil. He speculated that some organic substances form water soluble metallo-organic complexes. Other reviewers (Wallace,1962; Mortensen,1963; Lehman,1963) support the view that Fe-organic complexes exist in soils.

Information on the presence or extent of occurrence of Fe-organic complexes in reduced soils is limited. Even under upland conditions, the concentrations of water soluble Fe chelates have not been demonstrated satisfactorily.

For the right interpretation of analytical data in studying the physical chemistry of Fe in reduced soils, it is important to know how much of the Fe measured in soil solution can be attributed to organic complexes of Fe. The experimental findings of Olomu _et al_. (1973) and the general rule for the stability of metallic chelates provide some clues to this question.

Olomu _et al_. (1973) found that, in soils saturated with water and incubated, the concentration of the Fe-organic complex ranged from 0.0 to 3.3 ppm. This indicates that the concentration of water-soluble Fe existing as Fe-organic complexes may not be high.

It is a general rule that the stability of metal chelates is proportional to the magnitude of charge of the ion and to the reciprocal of ionic radius (Martell and Calvin,1962). From this rule it is expected that the stability of Fe^{++} -chelates would be smaller than that of Fe^{3+} -chelates, because Fe^{3+} is larger in charge and smaller in ionic radius than Fe^{++}. Practically reported stability constants support this rule (Wallace,1962, p.19 and 26).

Upon the ground of these points it seems probable that the concentration of Fe-chelates in reduced soils may not be too high.

Turning to the problem of ion-pairs, it is obvious that by correcting the concentration terms for both activity coefficients and ion-pairs, more refined information can be obtained (Adams,1971). But it seems likely that the correction for ion-pairs is not a matter of urgent necessity in studies of such a rough system as reduced soils. Adams (1971) presented an example of the correction for ion-pairs with $CaSO_4$ solution. According to his calculations the difference between the activities of Ca^{++} and $SO_4^{=}$ before and after the correction was at the level of $10^{0.1}M$. A difference of this magnitude does not seem to be a serious problem in dealing with reduced soils or muds. The experimental error usually exceeds this level. Accordingly, it is likely that neglecting the influence of chelates and ion-pairs of Fe will not give rise to critical error in describing the essential activity relations of Fe^{++} in reduced soils.

So, it appears useful to take the degree of reduction and the acidity of soils and the intensity of CO_2 as the essential parameters which determine the activity of Fe^{++} in the majority of reduced soils.

The influence of CO_2 in reduced soils on the activity of Fe^{++} has not been fully appreciated yet. According to Ponnamperuma _et al_. (1968), it is obvious that the pH of reduced soil is profoundly influenced by the intensity of CO_2. If so, it is to be expected that the occurrence of CO_2 will certainly influence the activity Fe^{++}. When the activity of Fe^{++} in reduced soils is assumed to be controlled by the redox couple, $Fe(OH)_3$-Fe^{++}, as Jeffery (1961) has suggested, the following redox equation defines the relationships among pE, pH and the activity of Fe^{++}:

$pE = 12.34 + pFe^{++} - 3pH$

However, if it is accepted that both pH and the activity of Fe^{++} are influenced by CO_2 it can be expected that, in reduced soils, the redox equation would be remarkably different from the above.

THEORETICAL STUDIES

A. Stability Fields for FeS and FeS_2 in pH-pE Diagrams for the Systems in Reduced Soils.

In studying the activity of H_2S in reduced soils, FeS has been regarded as the compound that controls the activity of aqueous sulfides. However, Garrels and Christ (1965, p 221, 223, 224) and Bostroem (1967) presented stability diagrams showing that the ranges of Eh-pH encountered in reduced soils are covered by FeS_2, suggesting that in the majority of reduced soils iron sulfide may exist mainly as FeS_2.

Pitts (1971) and Pitts et al. (1972b) presented stability relations on a pH-Eh diagram in which the area covering the pH range of 4 to 8 and the Eh range of -300 mv and above is entirely occupied to FeS_2. They maintained that, on the basis of this diagram, FeS_2 is an important component for study in the aqueous equilibria of sulfides in reduced soil systems.

If it is true that FeS_2 is the major iron sulfide species in reduced soils and that FeS_2 controls the activities of aqueous sulfides, FeS could have been eliminated in the consideration of sulfide equilibria in submerged soils. However, the commonly observed iron sulfide in freshly submerged soils is FeS; it is black in color and X-ray amorphous.

The following calculations give theoretical justification for the greater stability of FeS over FeS_2 in the ranges of pH and Eh in reduced soils.

In constructing a stability diagram, the selection of the activity of dissolved sulfides in the system is important. In aforementioned references, very high concentrations of dissolved sulfides were selected. The stability diagram that can be applied to reduced soil systems should select activities of dissolved sulfides that are expected to exist in the soil system.

Redox potential equation for $S_2^{--} - S^{--}$ couple: (From the free energy of formation, the E° or pE° value is found as follows with this equation)

$S_2^{--} + 2e = 2S^{--}$

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$\Delta F_r^\circ = 2.21$

$$E^\circ = \frac{-\Delta F_r^\circ}{n \times 23.06} = \frac{2.21}{46.12} = -0.048$$

Thus the redox potential equation is,

$$Eh = -0.048 - 0.059 \log S^{--} + 0.029 \log S_2^{--}$$

$$\text{or, } pE = -0.81 + pS^{--} - 1/2\ pS_2^{--} \quad \ldots\ldots\ldots\ldots\ldots \quad (43)$$

Because the activities of S^{--} and S_2^{--} are determined by the pH and the activities of Fe^{++}, to convert equation (43) into a pH-pE equation, it is necessary to have the solubility products of FeS and FeS_2. The solubility product of FeS is available but that of FeS_2 sould be calculated from the free energy of formation, as follows:

$FeS_2 = Fe^{++} + S_2^{--}$

-36.00 -20.30 19.75

$\Delta F_r^\circ = 35.45$

$$Ks = (Fe^{++})(S_2^{--}) = 10^{-25.98} \quad \ldots\ldots\ldots\ldots\ldots \quad (44)$$

From the solubility products of FeS and FeS_2, the ratio between (S^{--}) and (S_2^{--}) is found as follows:

$$\frac{(Fe^{++})\ (S^{--})}{(Fe^{++})(S_2^{--})} = \frac{10^{-18.40}}{10^{-25.98}} = 10^{-7.58}$$

or, $\log S_2^{--} = \log S^{--} - 7.58$ . . . . (45)

From the solubility product of FeS,

$\log S^{--} = -18.40 - \log Fe^{++}$ . . . .(46)

If the activity of Fe^{++} is assumed to be controlled by $FeCO_3$-H_2O-CO_2 system (in the pH range of 6.0 to 7.26),

$\log Fe^{++} \mathrel{\hat{=}} -0.3 - 1/2\ pH$ . . . . (47)

by combining the equations (46) and (47),

$\log S^{--} = 1/2\ pH - 18.10$ . . . .(48)

and by combining the equations (45) and (48)

$\log S_2^{--} = 1/2\ pH - 25.68$ . . . . (49)

When $\log S^{--}$ and $\log S_2^{--}$ in equation (43) are replaced by their equivalents from equations (48) and (49), we have

$pE = 4.45 - 1/2\ pH$ . . . . (50)

Equation (50), when depicted on a pE-pH diagram (Figure 1), divides the stability fields for FeS_2 and FeS over the pH range below 7.26 (the stability area for $FeCO_3$). The area above the line is the stability field for FeS_2 and below is for FeS.

In the case of alkaline conditions (above pH 7.26 or the stability field for $Fe_3(OH)_8$), $\log S^{--}$ and $\log S_2^{--}$ are respectively,

$\log S^{--} = -7.80 - 2\ pH$ . . . . (51)

and $\log S_2^{--} = -25.38 - 2pH$ . . . . (52)

Substitution of equations (51) and (52) for $\log S^{--}$ and $\log S_2^{--}$ in equation (43) yields following pH-pE equation.

$pE = 9.90 - pH$ . . . . (53)

Equation (53) divides the stability fields for FeS_2 and FeS, over the pH range above 7.26, as shown in Figure 1.

Figure 1 shows that in reduced soils where the activity of Fe^{++} is expected to be controlled b the $FeCO_3$-H_2O-CO_2 system or by the solubility of $Fe_3(OH)_8$, the formation of FeS is favored over that of FeS_2. On the basis of this theoretical consideration, it is possible to point out that, in studying the equilibria of aqueous sulfides in commonly occurring reduced soils, it is not necessary to take FeS_2 as a significant component.

B. Activity of H_2S and Fe^{++} in FeS Systems.

Iron sulfide (FeS) is usually formed in reduced soils. When FeS is brought into an aqueous system, FeS dissolves to produce Fe^{++}, H^+, $S^=$, HS^-, and H_2S, and the relationships among pH and the activities of Fe^{++} and H2S are defined by following equation:

$$pFe^{++} = 2pH - (pK_1+pK_2-pKs) - pH_2S \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (54)$$

where, $pX = -\log X$

$$K_1 = \frac{(HS^-)(H^+)}{(H_2S)} = 1.1 \times 10^{-7}$$

$$K_2 = \frac{(S^=)(H^+)}{(HS-)} = 1.1 \times 10^{-14}$$

$$Ks = (Fe^{++})(S^=) = 4 \times 10^{-19}$$

When the numerical equivalents are given to the respective constants,

$$pFe^{++} = 2pH - 2.56 - pH_2S \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (55)$$

Equation (55) is the one that has long been used in studying the FeS system. However, this equation involves three variables in one equation and does not provide straightforward information on the pH vs pH_2S, pH vs pFe^{++}, or pFe^{++} vs pH_2S relationships in the system $Fe^{++} - H^+ - S^= - HS^- - H_2S$.

Another type of pH-pH_2S equation is obtained by solving an equation of charge neutrality balance.

$$2(Fe^{++}) + (H^+) = (OH^-) + (HS^-) - 2(S^=) \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (56)$$

All the variables in equation (56) can be expressed in terms of (H^+) and (H_2S).

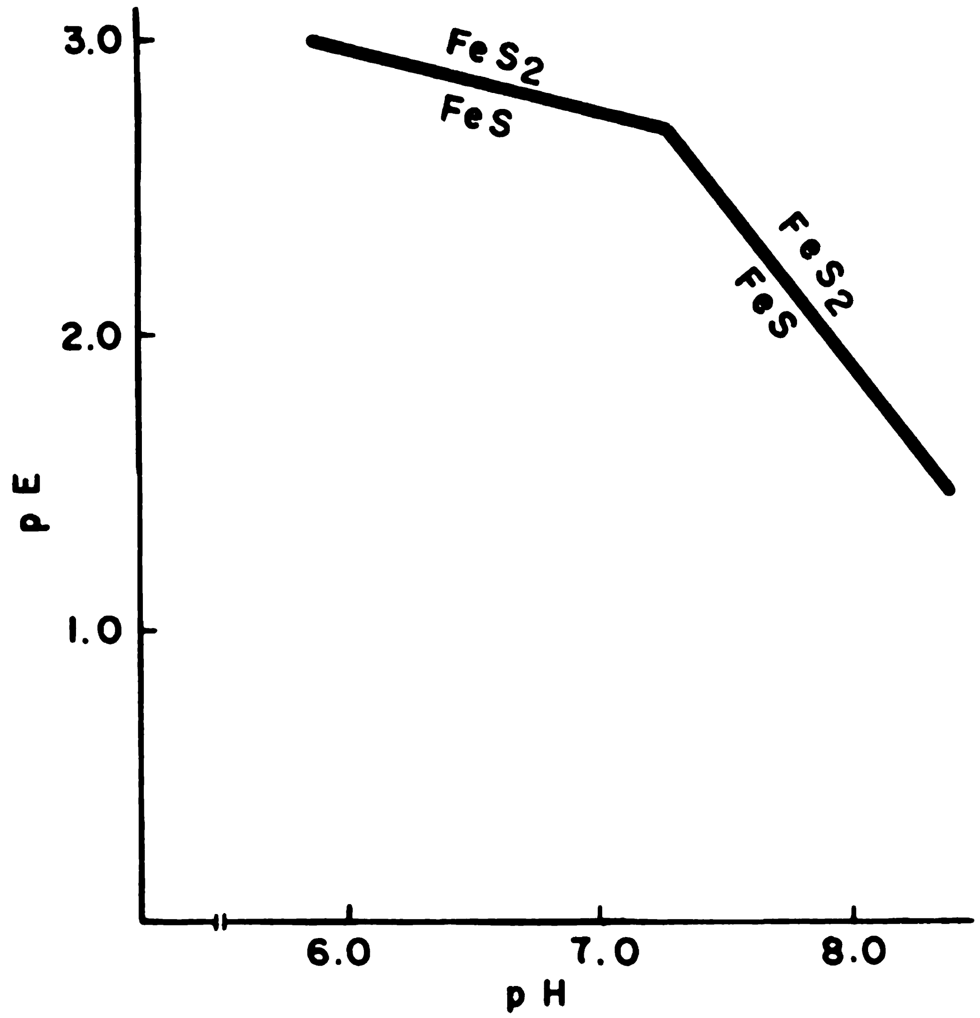


Figure 1. Stability fields for FeS and FeS_2 with respect to the pH and pE of the system.

$$2\frac{K_s(H^+)^2}{K_1K_2(H_2S)} + (H^+) = \frac{Kw}{(H^+)} + \frac{K_1(H_2S)}{(H^+)} + 2\frac{K_1K_2(H_2S)}{(H+)^2}$$

rearranging:

$$2K_s(H^+)^4 = -(H^+)^3K_1K_2(H_2S)$$

$$+\left[(H^+)K_1^2K_2 + 2K_1{}^2K_2^2\right](H_2S)^2$$

neglecting insignificant terms,

$$2K_s(H^+)^3 = K_1{}^2K_2\ (H_2S)^2$$

When the concentration terms are converted into activity terms and the activity coefficient of H^+ is taken as unity, inserting numerical values for constants yields the following:

$$pH = 3/2\ pH - 3.18 - 1/3\ (\log \gamma HS^- - \log \gamma Fe^{++})\ .\ .\ .\ .\ .\ \ (57)$$

$$\text{or}\ \ pH_2S = 3/2\ pH - 4.76 - 1/2\ (\log \gamma HS^- - \log \gamma Fe^{++})\ .\ .\ \ (58)$$

Equation (58) is the pH-pH_2S equation for FeS-H_2O-H_2S system. By combining this with equation (55) a pH-pFe^{++} equation is obtained as follows:

$$pFe^{++} = 1/2pH + 2.20 + 1/2(\log \gamma HS^- - \log \gamma Fe^{++})\ .\ .\ .\ .\ \ (59)$$

Equations (57) and (59) are the criteria for the identification of the system FeS-H_2O-H_2S. By measuring the pH and the activity of Fe^{++} in a system, it can be known whether the system FeS-H_2O-H_2S is operating or not.

C. Activity of Fe^{++} in the System $FeCO_3$-H_2O-CO_2.

Since reduced soils are in equilibrium with around 0.2 atm of CO_2, and since the pH of reduced soils is quantitatively correlated with the partial pressure of CO_2, it appears likely that the $FeCO_3$-H_2O-CO_2 system may operate in reduced soils. So, it is important to know the activity of Fe^{++} in such a system for the quantitative study of H_2S in reduced soils.

Ponnamperuma (1966) derived an equation for the system $FeCO_3$-H_2O-CO_2 in a way similar to that shown for the derivation of equations for FeS systems.

$$pFe^{++} = 2pH - 7.47 + \log PCO_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (60)$$

where PCO_2 is the partial pressure of CO_2.

He also derived a pH-PCO_2 equation for the same system.

$$pH = 5.19 - 2/3 \log PCO_2 + 1/3 (\log HCO_3^- - \log Fe^{++}) \quad \ldots\ldots \quad (61)$$

Equation (60) involves three variables in an equation, thus, it is a complicated equation for practical application. By combining equation (60) with (61) a much simpler pH-pFe^{++} equation is obtained.

$$pFe^{++} = 1/2pH + 0.3 + 1/2(\log\gamma HCO_3^- - \log\gamma Fe^{++}) \quad \ldots\ldots\ldots \quad (62)$$

Again, equations (61) and (62) are the criteria for the identification of the $FeCO_3$-H_2O-CO_2 system. It is remarkable to notice obvious differences in the coefficient for pH in the equations (60) and (62). In equation (60), the coefficient is 2, but in equation (62) it is 0.5. From equation (60) one may expect one unit of pH change would result in the change of the activity of Fe^{++} by hundred times. In equation (62) on the other hand, one unit of pH change means the change of the activity of Fe^{++} by 3.16 times.

The terms $\log \gamma HCO_3^-$ and $\log \gamma Fe^{++}$ will vary depending upon the ionic strengths of the system. But the magnitude of the term ($\log \gamma HCO_3^-$ - $\log \gamma Fe^{++}$) is not great. So, in the following discussions the terms will be neglected for simplicity. Thus, equation (62) will be written as,

$$pFe^{++} \triangleq 1/2\ pH + 0.3 \quad (63)$$

D. Activity of H_2S in $FeCO_3$-H_2O-CO_2-FeS-H_2S System.

If FeS or H_2S are introduced into an environment where the activity of Fe^{++} is determined by the system $FeCO_3$-H_2O-CO_2, the activity of H_2S may be expressed by equation (64) which is derived by combining equation (55) with (63):

$$1/2\ pH + 0.3 \triangleq 2pH - 2.56 - pH_2S$$

$$\text{or, } pH_2S \triangleq 3/2\ pH - 2.86 \quad (64)$$

E. Activity of H_2S in $Fe_3(OH)_8$-FeS-H_2O-H_2S System.

In a system where the activity of Fe^{++} is determined by the solubility of $Fe_3(OH)_8$, the activity of Fe^{++} is given as follows (Ponnamperuma 1955, 1965, 1972a):

$$pFe^{++} = 2pH - 10.6 \quad (65)$$

In the system where $Fe_3(OH)_8$ and FeS exist simultaneously, the activity of H_2S may be given as follows, combining equations (55) and (65):

$$2pH - 10.6 = 2pH - 2.56 - pH_2S$$

$$\text{or, } pH_2S = 8.04 \quad (66)$$

Ponnamperuma (1966) considered that the bulk of ferrous iron in reduced soils exists as $Fe_3(OH)_8$, and this is the compound that may control the activity of Fe^{++} in ferruginous reduced soils. If this is true, equation (66) says that the activity of H_2S in such soils should be constant at the level of $10^{-8.04}$ M, regardless of the pH of the system.

F. Activity of H_2S in the System of $Fe_3(OH)_8$-CO_2-H_2O-FeS-H_2S.

Ponnamperuma et al. (1968) demonstrated that the introduction of CO_2 into an aqueous suspension of $Fe_3(OH)_8$ influences the pH of the system remarkably. However, they did not study the influence of CO_2 on the activity of Fe^{++} in their $Fe_3(OH)_8$ system.

From equations (63) and (65) it is obvious that, at the lower pH's, the activity of Fe^{++} from $FeCO_3$ is much lower than that from $Fe_3(OH)_8$. This indicates that the introduction of CO_2 to $Fe_3(OH)_8$ system would influence the activity of Fe^{++} remarkably. From the following calculations the stability fields for $FeCO_3$ and $Fe_3(OH)_8$ can be predicted.

$1/2 \text{ pH} + 0.3 = 2\text{pH} - 10.6$

or, $\text{pH} = 7.26$

This shows that, when CO_2 is introduced into the $Fe_3(OH)_8$ system, in the pH range below 7.26 $FeCO_3$ dominates and in the pH range above 7.26, the $Fe_3(OH)_8$ will dominate. It also is likely that, even with $FeCO_3$, when the pH is raised by adding alkali into the alkaline range, $FeCO_3$ may lose its stability.

In other words, in the system $Fe_3(OH)_8$-H_2O-CO_2, the activity of Fe^{++} will be determined by the $FeCO_3$-H_2O-CO_2 system at pH ranges below 7.26 and, in the pH range above 7.26, the activity of Fe^{++} will be determined by the solubility of $Fe_3(OH)_8$.

Accordingly, the activity of H_2S in the system $Fe_3(OH)_8$-CO_2-H_2O-FeS-H_2S, will be determined by equation (64), ($pH_2S \triangleq 3/2 \text{ pH} - 2.86$), in the pH range below 7.26 and by the equation (66) ($pH_2S = 8.04$) above pH 7.26. Figure 2 shows these relationships.

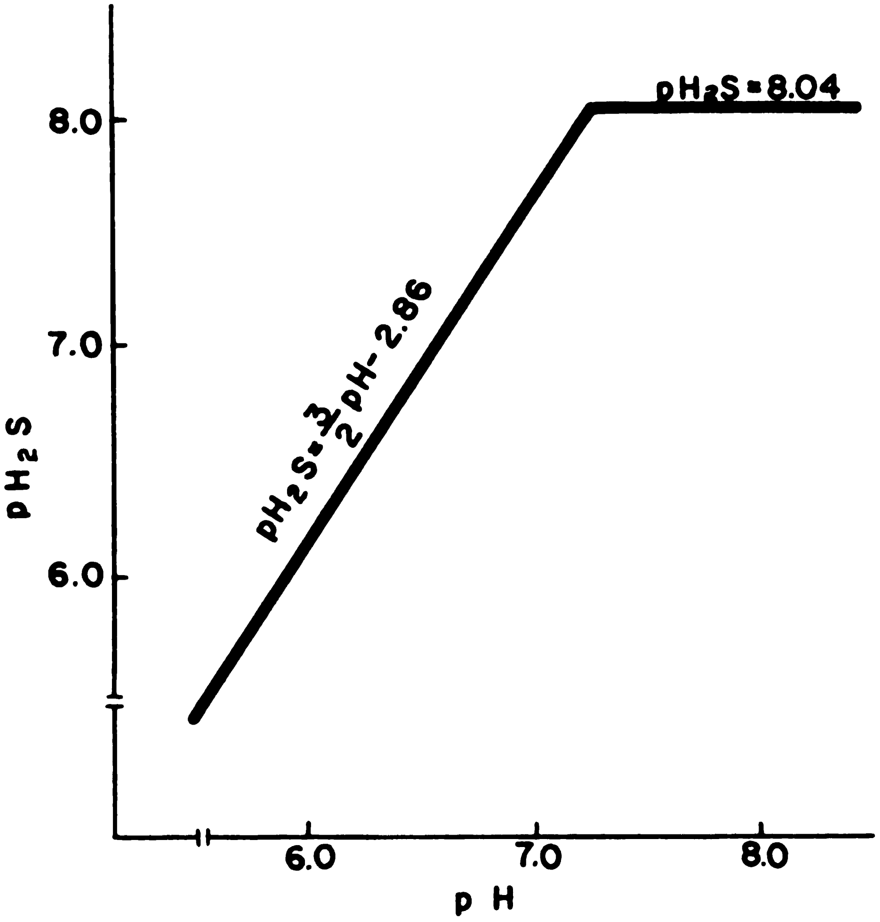


Figure 2. Theoretical pH-pH$_2$S relationships for the system FeCO$_3$-H$_2$O-CO$_2$-FeS-H$_2$S and Fe$_3$(OH)$_8$-FeS-H$_2$O-H$_2$S.

EXPERIMENTS

A. Experiment I

- pH -pFe^{++} Relationship in $FeCO_3$-H_2O-CO_2 System -

1. Objective: The objective of this experiment was to test the validity of the equation,

$$pFe^{++} \hat{=} 1/2\ pH - 0.3,$$

in the $FeCO_3$-H_2O-CO_2 system. It was also intended to test the possibility of the generalization of the equation as $pM^{++} = 1/2\ pH + K$ for the systems MCO_3-H_2O-CO_2, (where M is the metal ion). Thus, in addition to $FeCO_3$-H_2O-CO_2, the system $CaCO_3$-H_2O-CO_2 was also studied.

2. Methods

$FeCO_3$-H_2O-CO_2 system: $FeCO_3$ suspension was prepared by the method described by Ponnamperuma *et al*. (1968). The solution of 0.05 M $FeSO_4.7H_2O$ was reacted with 0.05 M Na_2CO_3 in a reaction vessel equipped with electrodes for pH measurements, electrical conductivity cell, and inlet and outlet for gases (Fig. 3). The reaction was carried out in the absence of O_2, and the suspension was bubbled with pure CO_2 gas. A pale greenish gray precipitate was obtained.

Equilibria under different partial pressures of CO_2 were obtained by keeping the suspension under gas compositions which varied from 0.01% to 100% CO_2 in pure N_2 gas. A 3 to 8-hour reaction time was given to obtain equilibria depending upon the partial pressure of CO_2. In the equilibrated system, pH and EC were measured. A portion of suspension taken from the equilibrated system was filtered and analysed for Fe^{++} by colorimetry, with the aid of o-phenanthroline. The ionic strength of each system was calculated from the specific conductance (k), using the following equation

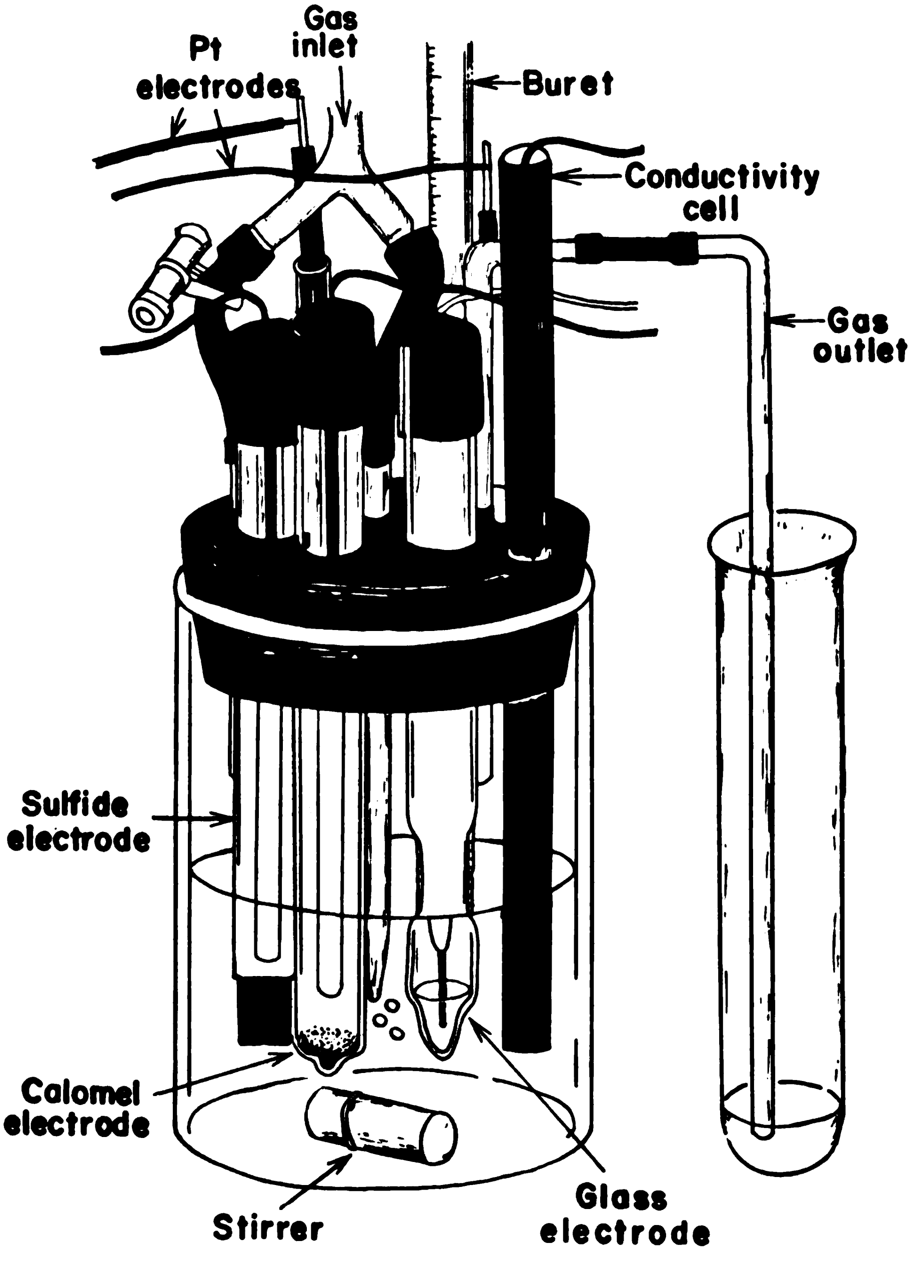


Figure 3. The equilibration vessel.

suggested by Ponnamperuma et al. (1966b).

$$\mu = 6 \times 10^{-4} + 14.7k + 3096\ k^2$$

where, μ is the ionic strength and k is the activity coefficient of Fe^{++} taken from the table presented by Killand (1937).

$CaCO_3$-H_2O-CO_2 system: Suspensions of $CaCO_3$ containing 0.5g of of analytical grade $CaCO_3$ in 100 ml of distilled water were prepared in the reaction vessel used in the study of $FeCO_3$ systems.

To obtain the equilibria under different partial pressures of CO_2, air-CO_2 mixtures with varying composition of CO_2 (0.03% to 100% CO_2) were bubbled into the suspension with gentle stirring. In the equilibrated system, pH and electrical conductivity were measured, and a portion of suspension was pipetted, filtered and analysed for Ca^{++} by atomic absorption spectrophotometry.

The activity coefficients for Ca^{++} were calculated from the electrical conductivities in the manner described in the foregoing section. But for the conversion of electrical conductivity to ionic strength, the following equation suggested by Ponnamperuma et al. (1966) was used.

$$\mu = 15.11\ k + 21.86\ k^2$$

3. Results and Discussion

As shown in Figure 4 the experimentally obtained pH-pFe^{++} equation is,

$$pFe^{++} = 0.56\ pH - 0.042 \quad \ldots\ldots\ldots\ldots \quad (67)$$

Although there is some deviation both in the slope and intercepts, equation (67) is fairly close to the theoretical equation, proving the validity of the theoretical approach for the derivation of this equation. The deviations might be due to the possible presence of ion pairs of $FeCO_3$ and $Fe(HCO_3)_2$ (Adams 1971) and the presence of heterogeneous salts such as hydroxycarbonates of Fe (Schindler 1967).

For the system $CaCO_3$-H_2O-CO_2, the theoretical pH-pCa^{++} equation derived as in the case of the $FeCO_3$-H_2O-CO_2 system is

$$pCa^{++} \triangleq 1/2\ pH - 0.85 \quad \ldots \quad (68)$$

The experimentally obtained equation is also fairly close to the theoretical one.

So, it is concluded that the theoretical pH-pFe^{++} and pH-pCa^{++} equations for the respective systems, $FeCO_3$-H_2O-CO_2 and $CaCO_3$-H_2O-CO_2, are valid. This also indicates that this type of equation can be applicable for other sparingly soluble metallic carbonates.

B. Experiment II

- pH-pFe^{++} Relationships in Reduced Soils -

1. Objective:

In reduced soils, CO_2 accumulates to levels which can influence the activity of Fe^{++} by forming $FeCO_3$. If it is admitted that the occurrence of $FeCO_3$ in reduced soils is a matter of reality, it will be natural to expect that the activity of Fe^{++} in such a system would be controlled by the system $FeCO_3$-H_2O-CO_2. The primary objective of this experiment was to investigate the pH-pFe^{++} relationships in some ferruginous acidic paddy soils under submerged condition. It was also intended to look into the relationship between the active iron contents of soils and the pH of the reduced soils.

2. Materials and Methods

(a) Materials:

Fifteen randomly selected acid alluvial paddy soils, which are the most commonly occurring in Korean paddy fields, containing 0.4 to 1.6% of active iron analysed by Asami and Kumada method (1969), were used for the study.

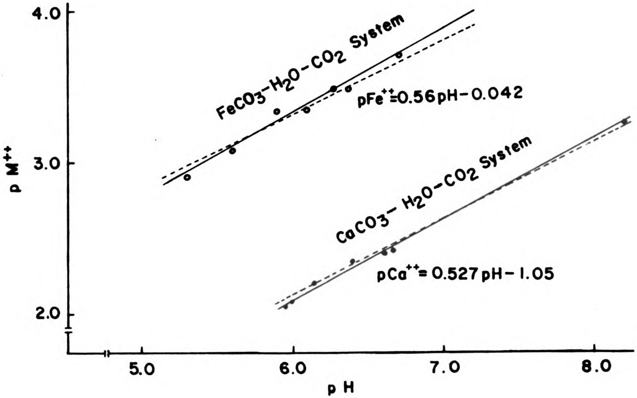


Figure 4. pH-pM^{++} relationships for the systems $CaCO_3$-H_2O-CO_2 and $FeCO_3$-H_2O-CO_2. Solid lines are for the empirical equations and the dashed lines for the theoretical equations.

(b) Methods:

100 g of air-dried soils were submerged in 250 ml of distilled water in glass bottles. The submerged soils were incubated at 30°C for 6 weeks. At the end of the incubation period, the solution overlying the soils was decanted. The pH and the electrical conductivity were measured in soil slurry. A 20g portion of soil slurry was transferred to a centrifuge tube. he tube was stoppered and centrifugated at 10,000 rpm for 10 minutes at 0°C. Ferrous iron in the supernatant was analysed by colorimetry, using 0-phenanthroline. The ionic strengths of solutions were calculated from the electrical conductivity data as suggested by Ponnamperuma et al. (1966).

3. Results and Discussion

The analytical data are shown in Table 1 and the pH-pFe^{++} relations are depicted in Figure 5.

As shown in Table 1, the pH of the reduced soils tended to be higher in the soils which had higher active Fe contents. It is interesting to see that the activity coefficients for Fe^{++} do not vary widely, in spite of the wide range in pH of the soils. The average value of the activity coefficient was 0.69 and its standard deviation was found to be fairly small (0.03). Thus it seems likely that the value of 0.7 for the activity coefficient of Fe^{++} may be used as an average value in ferruginous reduced soils.

The relationship between pH and the activity of Fe^{++} is shown to be fairly close to that of the $FeCO_3$ system (Figure 4). This result convincingly demonstrates that the activity of Fe^{++} is not controlled by either the FeS-H_2O-H_2S system or the solubility of $Fe_3(OH)_8$.

Table 1. The active Fe contents of air-dried soils, and pH, electrical conductivities and pFe^{++} of reduced soils.

Soils	Active Fe (%)	pH	EC mmho	$(Fe^{++})^1 \times 10^3$	γFe^{++2}	pFe^{++}
1	0.39	6.2	0.77	0.99	0.65	3.19
2	0.49	6.3	0.37	0.75	0.73	3.26
3	0.47	6.3	0.67	1.05	0.67	3.15
4	0.45	6.1	0.37	0.93	0.73	3.17
5	0.72	6.9	0.63	1.16	0.68	3.55
6	0.78	6.2	0.61	1.12	0.68	3.15
7	0.87	6.2	0.50	1.40	0.71	3.00
8	0.92	6.7	0.59	0.51	0.69	3.51
9	0.91	6.3	0.44	0.83	0.72	3.22
10	0.92	7.0	0.28	0.81	0.76	3.21
11	0.71	6.3	0.53	0.58	0.70	3.39
12	0.54	6.5	0.63	1.12	0.68	3.12
13	0.98	6.8	0.72	0.58	0.68	3.40
14	0.66	6.9	0.80	0.46	0.65	3.32
15	1.60	6.8	0.74	0.44	0.66	3.54

[1] Concentration of Fe^{++} in mol/l

[2] Activity coefficient of Fe^{++}

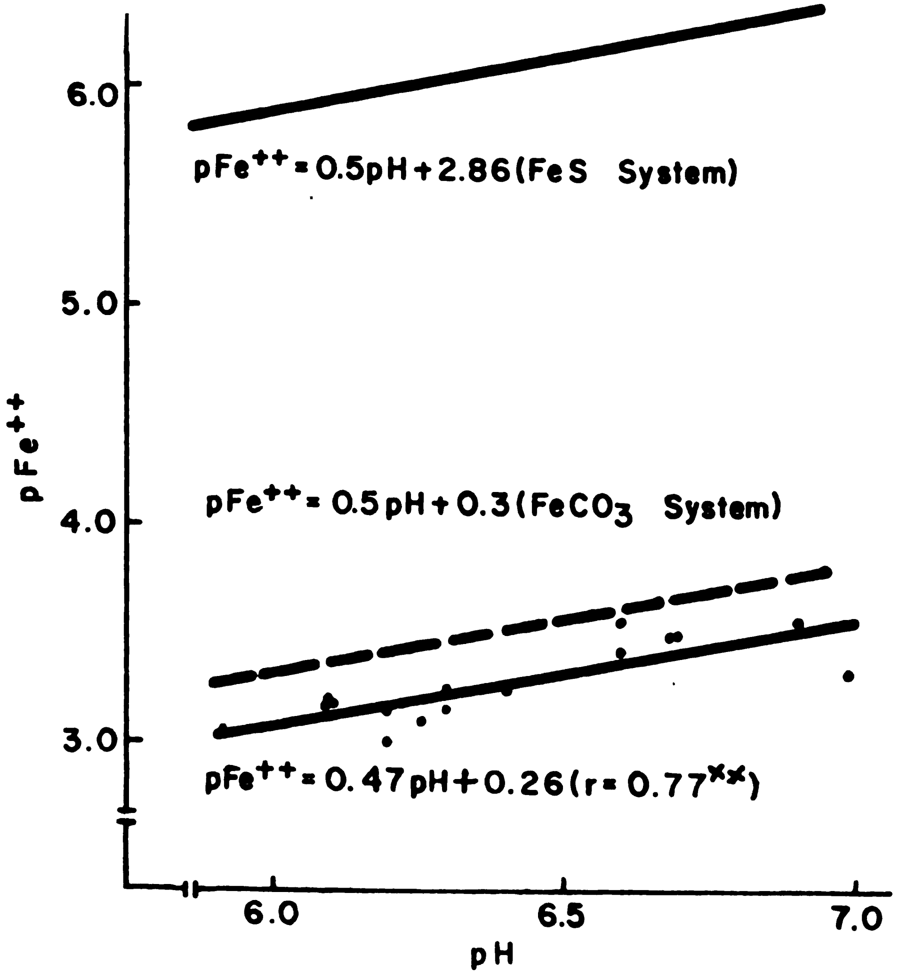


Figure 5. pH-pFe^{++} relationships for the reduced soil systems compared with the theoretical pH-pFe^{++} relationships for the systems $FeCO_3$-H_2O-CO_2 and FeS-H_2O-H_2S.

C. Experiment III

- Activity of H_2S in Various Systems of Iron Hydroxides, Iron Carbonate and Reduced Soils -

1. Objective:

It is known that the pH-pFe^{++} relationships in iron hydroxide systems are different from that in the iron carbonate system. Accordingly, it is expected that the pH-pH_2S relationships in the iron carbonate system would be different from those in iron hydroxide systems. It is also known that the pH-pFe^{++} relationships among the different iron hydroxide systems are different. For example, the pH-pFe^{++} relationship is pFe^{++} = 2pH - 13.2 (Latimer, 1952) in the $Fe(OH)_2$ system, and pFe^{++} = 2pH - 10.8 (Ponnamperuma, 1972a) in the $Fe_3(OH)_8$ system. Consequently, the pH-pH_2S relationships among the different iron hydroxide systems are expected to be different. $Fe_3(OH)_8$ which has been considered as the principal factor that controls the activity of Fe^{++} in reduced soils (Ponnamperuma, 1965, 1972a, b) is a very unusual compound. In the sense of stoichiometry, $Fe_3(OH)_8$ may be considered as an admixture of two molecules of $Fe(OH)_3$ and one molecule of $Fe(OH)_2$. Theoretically, this compound should be prepared by alkalizing the solution containing Fe^{3+} and Fe^{++} at a ratio of 2 to 1. However, Ponnamperuma, Castro and Valencia (1968) prepared this compound by alkalizing a solution containing Fe^{3+} and Fe^{++} at a ratio of 1 to 2.5. A satisfactory explanation for this apparent discrepancy has not been presented. It would be worthwhile to obtain some information on just what types of iron hydroxides would be formed when varying proportions of Fe^{3+} and Fe^{++} were mixed and alkalized, and what the pH-pH_2S relationships in such systems would be.

The overall objective of the present experiments was to obtain quantitative information on the activities of H_2S in systems containing those Fe compounds which might be expected to occur in reduced soils.

The specific objectives of each experiment were 1) to determine the pH-pH_2S relationships in the systems iron hydroxide-FeS, $FeCO_3$-FeS, and iron hydroxide-$FeCO_3$-FeS, 2) to investigate the characteristics of Fe compounds formed under varying ratios of Fe^{3+} and Fe^{++}, and 3) to examine the effect of CO_2 on the pH-pH_2S and pH-pE relationships in the iron hydroxide systems.

2. Materials and Methods

(a) Materials:

i) Iron hydroxides: Different forms of iron hydroxides were prepared under a N atmosphere in the vessel used in Experiment I (Figure 3), by alkalizing solutions containing different amounts of Fe^{3+} as $Fe_2(SO_4)_3$ and Fe^{++} as $FeSO_4$, in ratios of 1:4, 1:2, 1:1, 2:1 and 3:1. The concentrations of the Fe solutions were both 0.05M.

ii) Soils: Two alluvial paddy soils, having active Fe and organic matter contents of 1.6% and 2.6% (soil 1) and 0.4% and 1% (soil 2) respectively, were used for the study.

(b) Methods:

i) pH-pH_2S and pH-pE relationships in iron hydroxide systems: To the iron hydroxide systems (pH = 10), 1 ml of 0.001M Na_2S was added which is approximately equivalent to 5 ppm of sulfide. Then the system was titrated with 0.5N H_2SO_4 to obtain different pH values. Following the addition of each increment of H_2SO_4, the sulfide potential ($E_{s^{--}}$), redox potential (Eh), and pH were measured. The $E_{s^{--}}$ was measured by a sulfide sensitive electrode which had been prepared by coating a silver electrode with silver sulfide (Ag_2S). From the E_s-- values the activity of H_2S was calculated as described by Berner (1963) and Ayotade (1972). The entire procedure was carried out under a N atmosphere.

ii) pH-pH_2S and pH-pE relationships in iron carbonate systems: Iron carbonate suspension was prepared as described in Experiment I. Exactly similar procedures were followed as in the case of iron hydroxide systems, except that the titrant used for this experiment was 0.5<u>N</u> NaOH.

iii) pH-pH_2S and pH-pE relationships in reduced soil systems: For the soils incubated under submerged condition at 30°C for six weeks, measurements were made for E_s--, Eh and pH, titrating with 0.5<u>N</u> NaOH.

3. Results and Discussion

(a) Iron Hydroxide Systems

(1) pH-pH_2S Relationships

pH-pH_2S relationships in the various iron hydroxide systems are depicted on Figure 6. As was expected, the pH-pH_2S relationships are different from system to system. It is very interesting to notice that the activity of H_2S is higher (smaller in pH_2S) in the iron hydroxide from 1:4 mixture of Fe^{3+} and Fe^{++}. When the fact is considered that more ferrous iron is given to this system, it is to be expected that the activity of H_2S in this system would be lower than the other systems. No systems behave exactly corresponding to $Fe_3(OH)_8$ system, which demands the theoretical pH-pH_2S relationships, $pH_2S = 8.02$. Only the 1:1 mixture of Fe^{3+} and Fe^{++} shows more or less constant pH_2S values regardless of pH.

However, the pH_2S value is smaller than 8.02, indicating that the activity of Fe^{++} in this system is lower than that in the $Fe_3(OH)_8$ system.

(2) pH-pE Relationships

Figure 7 depicts the pH-pE relationship in different iron hydroxide systems. The pH-pE equations obtained from the experimental results are summarized in Table 2. It is found that the iron hydroxide systems containing a 1:4 and a 1:2 mixture of Fe^{3+} and Fe^{++} are more or less similar in pH-pE relationships, but very different from the other two systems. This indicates that distinctly different redox couples of Fe were in operation in the two groups. It is possible to identify the redox couples operating in each system by comparing with the pH-pE relationships of known systems.

From the pH-Eh-pFe equations for various systems of iron oxides and iron hydroxides given by Garrels and Christ (1965) and Ponnamperuma et al. (1967), the following pH-pE-pFe^{++} equations are derived.

$Fe_2O_3-Fe^{++}$: $pE = 12.34 + pFe^{++} - 3pH$ . . . . . (77)

$Fe_3O_4-Fe^{++}$: $pE = 16.66 - 1.5pFe^{++} - 4pH$ . . . . (78)

$Fe(OH)_3-Fe^{++}$: $pE = 17.93 + pFe^{++} - 3pH$ . . . . . (79)

$Fe_3(OH)_8-Fe^{++}$: $pE = 23.27 + 1.5pFe^{++} - 4pH$ . . . . (80)

$Fe(OH)_3-Fe_3(OH)_8$: $pE = 7.26 - pH$ . . . . (81)

$Fe(OH)_3-Fe(OH)_2$: $pE = 4.63 - pH$ . . . . (82)

$Fe_3(OH)_8-Fe(OH)_2$: $pE = 3.31 - pH$ . . . . (83)

From the stability diagrams for different Fe compounds depicted by the aforementioned workers, it is found that equations (77), (78), (79) and (80) are for the acidic pH ranges, and equations (81), (82)

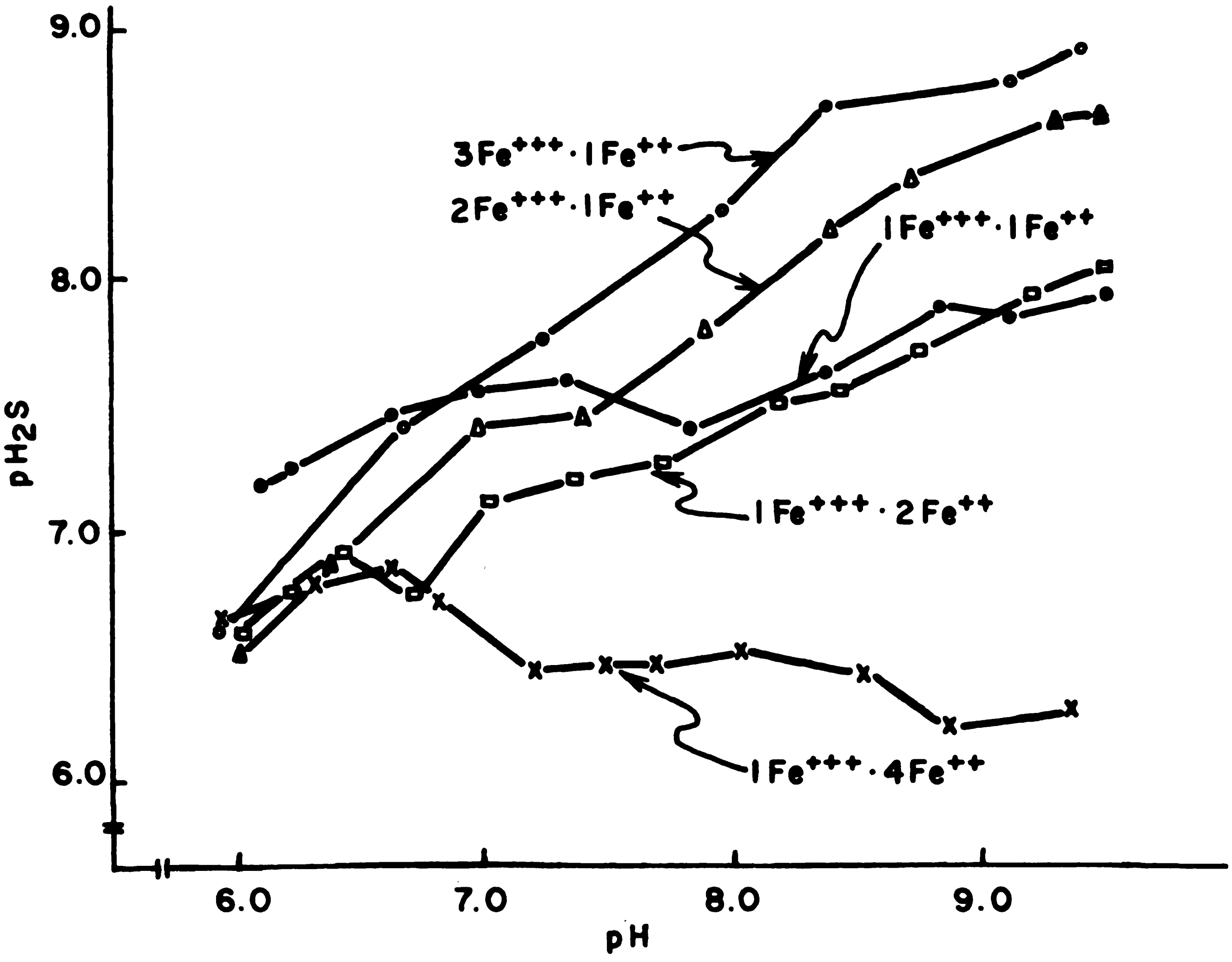


Figure 6. pH-pH_2S relationships for the systems involving mixtures of Fe^{+++} and Fe^{++} with different mixing rates.

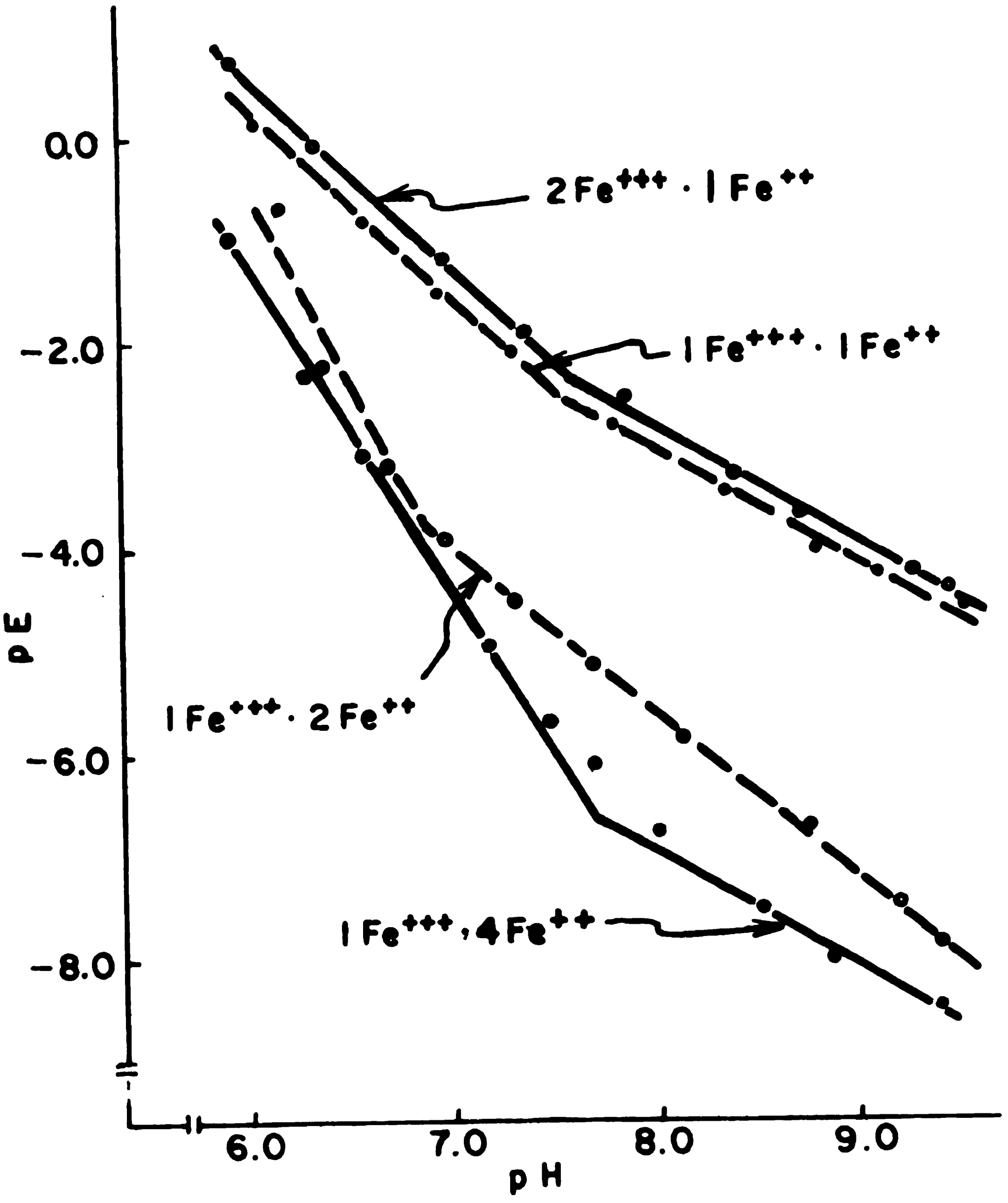


Figure 7. pH-pE relationships for the system involving mixtures of Fe^{+++} and Fe^{++} with different mixing rates.

Table 2. pH-pE relationships in the iron hydroxide systems prepared from the mixtures of Fe^{3+} and Fe^{++} with varying ratios.

Ratio of Fe^{3+} and Fe^{++}	Acidic system	Alkaline system
1 : 4	pE = 17.84-3.17 pH (69)[1]	pE = 6.08-1.59 pH (70)
1 : 2	pE = 18.39-3.20 pH (71)	pE = 7.35-1.61 pH (72)
1 : 1	pE = 11.40-1.85 pH (73)	pE = 4.45-0.96 pH (74)
2 : 1	pE = 11.61-1.83 pH (75)	pE = 5.63-1.06 pH (76)

[1] Numbers in the parentheses are the equation numbers

and (83) are for alkaline pH ranges. So, the equations for acid systems in Table 2 should be compared with the former group of equations and the equations for alkaline systems with the latter groups.

However, equations (69), (71) and (73) are not directly comparable with equations (77), (78), (79) and (80) because equation (69) is a pH-pE equation while equation (77) is a pH-pE-pFe^{++} equation, for example. But equations (70), (72), (74) and (76) are directly comparable with equations (81), (82) and (83) because they are in the same form. To make it possible to compare equation (77) with equation (69), it is necessary to transform equation (77) to the form of a pE-pH equation.

Equation (77) can be transformed into a pH-pE equation, by substituting the term pFe^{++} with a pH term. For instance, if the Fe^{++} in the system is equilibrated with H_2S and FeS, as in the present experimental systems, the pH-pFe^{++} relationship is given by equation (59), as

$$pFe^{++} \triangleq 0.5\ pH + 2.20$$

By combining equation (59) with equation (77),

$$pE = 14.50 - 2.5\ pH \ldots\ldots \quad (84)$$

In similar manner, equations (78), (79) and (80) are transformed as follows:

Equation (78) : $pE = 19.96 - 3.25\ pH$ . . . . (85)
Equation (79) : $pE = 20.13 - 2.5\ pH$ . . . . (86)
Equation (80) : $pE = 27.57 - 3.25\ pH$ . . . . (87)

Then it is possible to compare the experimentally obtained equations (69), (71) and (73) with these theoretical equations.

It is found that the equations (69) and (71) are more or less close to the equation (85), both in their intercepts and slopes.

So, it seems likely that in the systems of 1:4 and 1:2 mixture of Fe^{3+} and Fe^{++}, under acidic conditions, Fe_3O_4-Fe^{++} couple, instead of $Fe_3(OH)_8$-Fe^{++} couple, was in operation. In the alkaline condition, by comparing equations (70) and (72) with the theoretical equations (81), (82) and (83), it is found that the systems under investigation resemble none of the theoretically known systems.

In the 1:1 and 2:1 mixtures of Fe^{3+} and Fe^{++}, pH-pE relationships were far from any theoretically known systems in acidic pH ranges, while in alkaline pH ranges they were close to the redox couple of $Fe(OH)_3$-$Fe(OH)_2$.

In earlier discussion, it was pointed out that the preparation of $Fe_3(OH)_8$ is not easy. In alkaline condition, it may be formed easily. But under acidic conditions, it seems that Fe_3O_4 is more stable than $Fe_3(OH)_8$. Accordingly, in paddy soils in the normal pH range of 6.0 to 7.0, the occurrence of $Fe_3(OH)_8$ may not be common.

(b) pH-pH_2S and pH-pE Relationship in Iron Carbonate System

The pH-pH_2S and pH-pE relationships in the system $FeCO_3$-H_2O-FeS-H_2S are depicted in Figure 8 and Figure 9, respectively. In the pH range below 7.0 the experimentally obtained pH-pH_2S equation is:

$$pH_2S = 1.52\ pH - 3.15 \quad \ldots\ldots \quad (88)$$

Equation (88) is comparable with equation (64) which is the theoretical pH-pH_2S relationship in the system $FeCO_3$-H_2O-CO_2-FeS-H_2S. Between the two equations, there are some differences both in slope and intercepts. However, the deviation in the slope is not great. The difference in the intercepts seems not to be negligible. The reason for this may be found through studying the characteristics of the Fe compounds existing in the iron carbonate system.

From the following empirically obtained pH-pE equations it can be

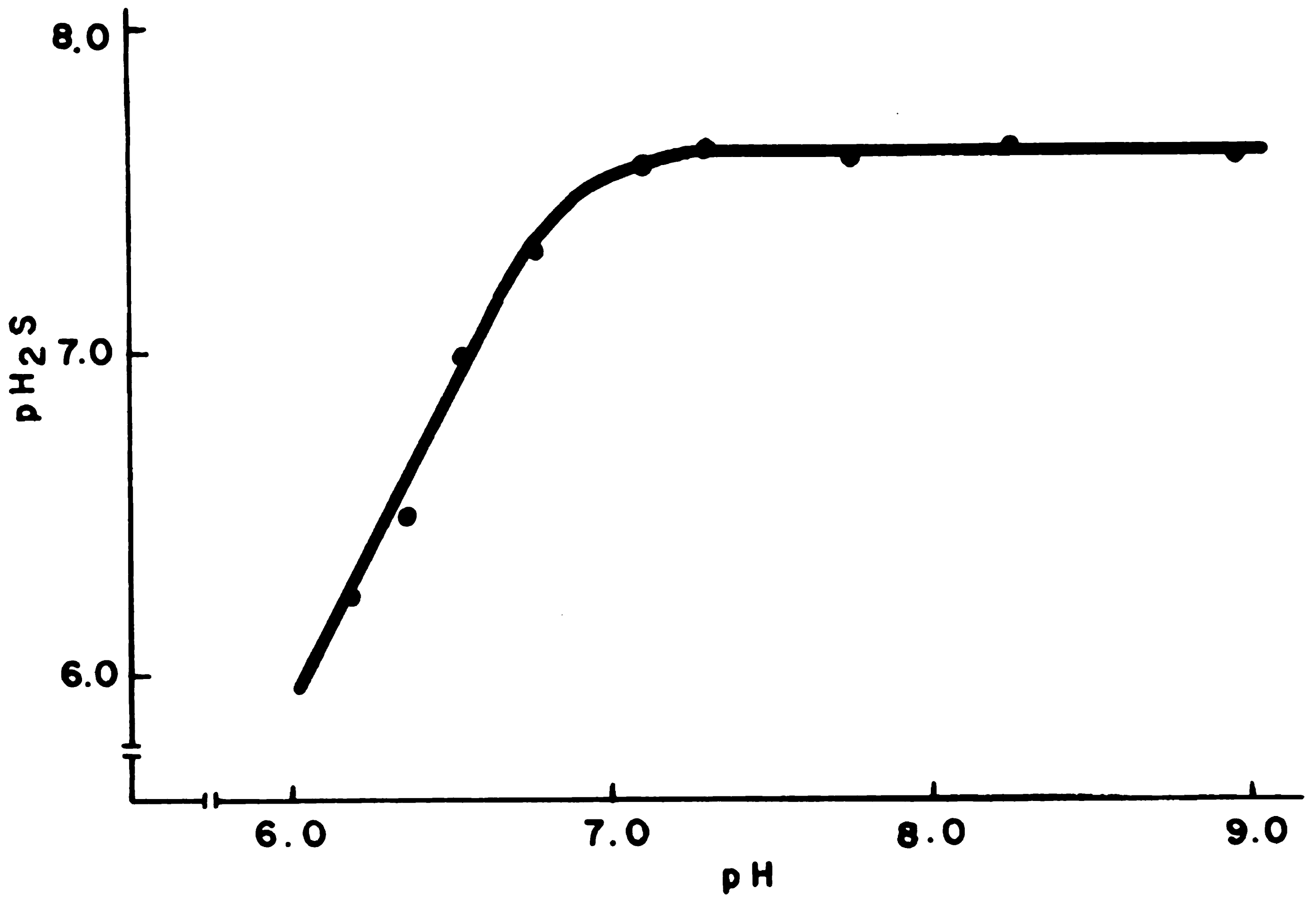


Figure 8. pH-pH_2S **relationship** for the $FeCO_3$-H_2O-CO_2-FeS-H_2S system.

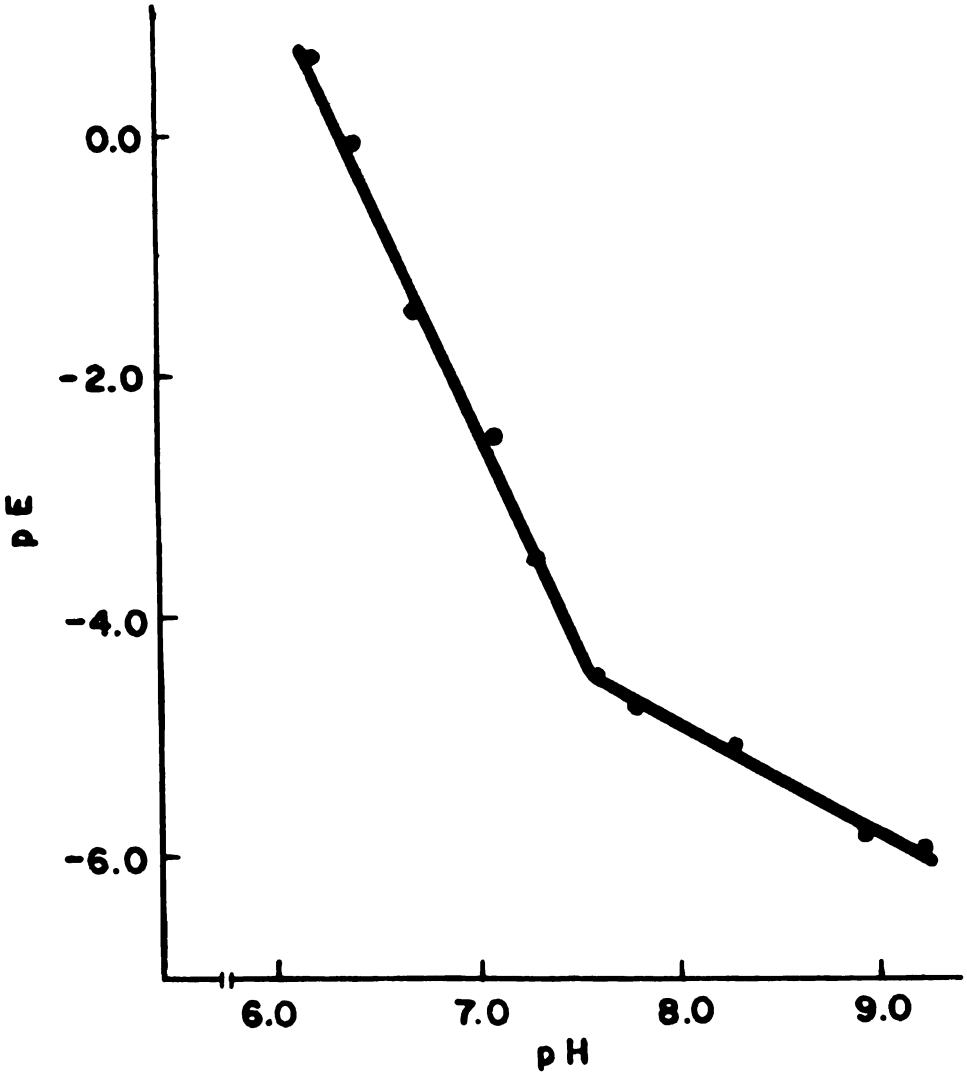


Figure 9. pH-pE relationship for the $FeCO_3$-H_2O-CO_2-FeS-H_2S system.

pointed out that in the acidic pH range, the Fe compound existing with $FeCO_3$ was Fe_3O_4. In the alkaline condition, the pE-pH equation did not correspond to any of the theoretically known hydroxide systems:

In acidic system : $pE = 22.91 - 3.59\ pH$ . . . . (89)

In alkaline system : $pE = 0.96 - 6.77\ pH$ . . . . (90)

(c) Influence of CO_2 on the pH-pH_2S and pH-pE Relationship in Mixtures of Fe^{3+} and Fe^{++}.

The influence of CO_2 on the pH-pH_2S and pH-pE relationship in systems containing 1:1 and 2:1 mixtures of Fe^{3+} and Fe^{++} are presented in Figures 10, 11, 12 and 13.

Remarkable effects of introducing CO_2 on the pH-pH_2S and pH-pE relations were observed. In both systems, the introduction of CO_2 decreased the activity of H_2S. It was observed that the pH-pH_2S relationship in 1:1 and 2:1 mixtures of Fe^{3+} and Fe^{++} under CO_2 treatment tended to shift to that of the iron carbonate system. In the pH-pE relationship, basically there was no change due to the introduction of CO_2. But it was observed that the introduction of CO_2 into the 1:1 mixture of Fe^{3+} and Fe^{++} increased the pE values. On the contrary, the addition of CO_2 to the 2:1 mixture of Fe^{3+} and Fe^{++} lowered the pE values.

These experimental results suggest that the presence of CO_2 in reduced Fe systems influences the activity relationships of Fe^{++} remarkably. It is interesting to notice that in the 2:1 mixture of Fe^{3+} and Fe^{++} the influence of CO_2 was less profound than in the 1:1 mixture. It may be reasoned that in the former system the activity of Fe^{++} was too low to be influenced by the presence of CO_2.

(d) pH-pH_2S and pH-pE Relationships in Reduced Soil Systems

Figures 14 and 15, respectively, show the relationships of pH-pH_2S and

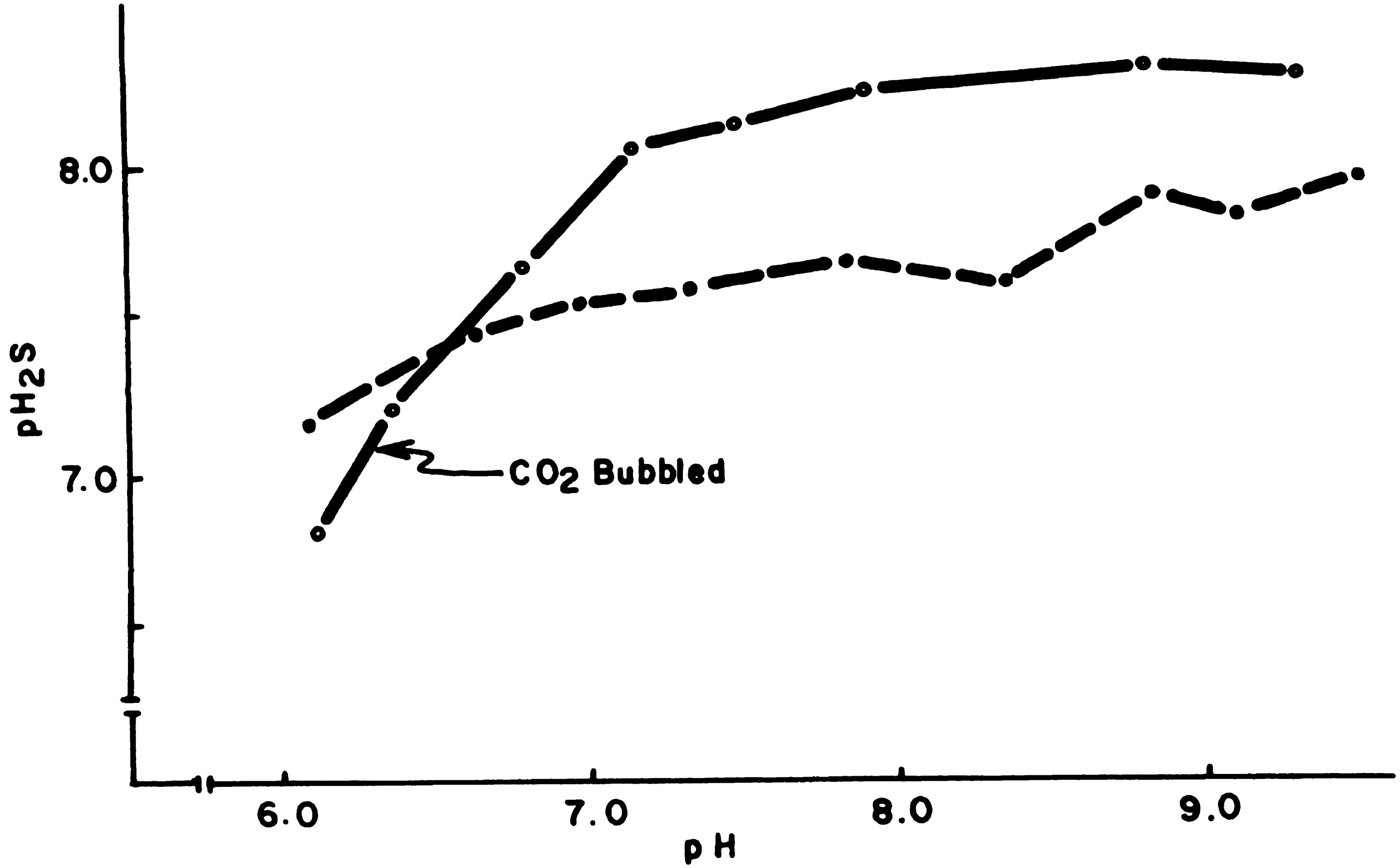


Figure 10. Effect of CO_2 on the pH-pH_2S relationship for the system involving a 1:1 mixture of Fe^{+++} and Fe^{++}.

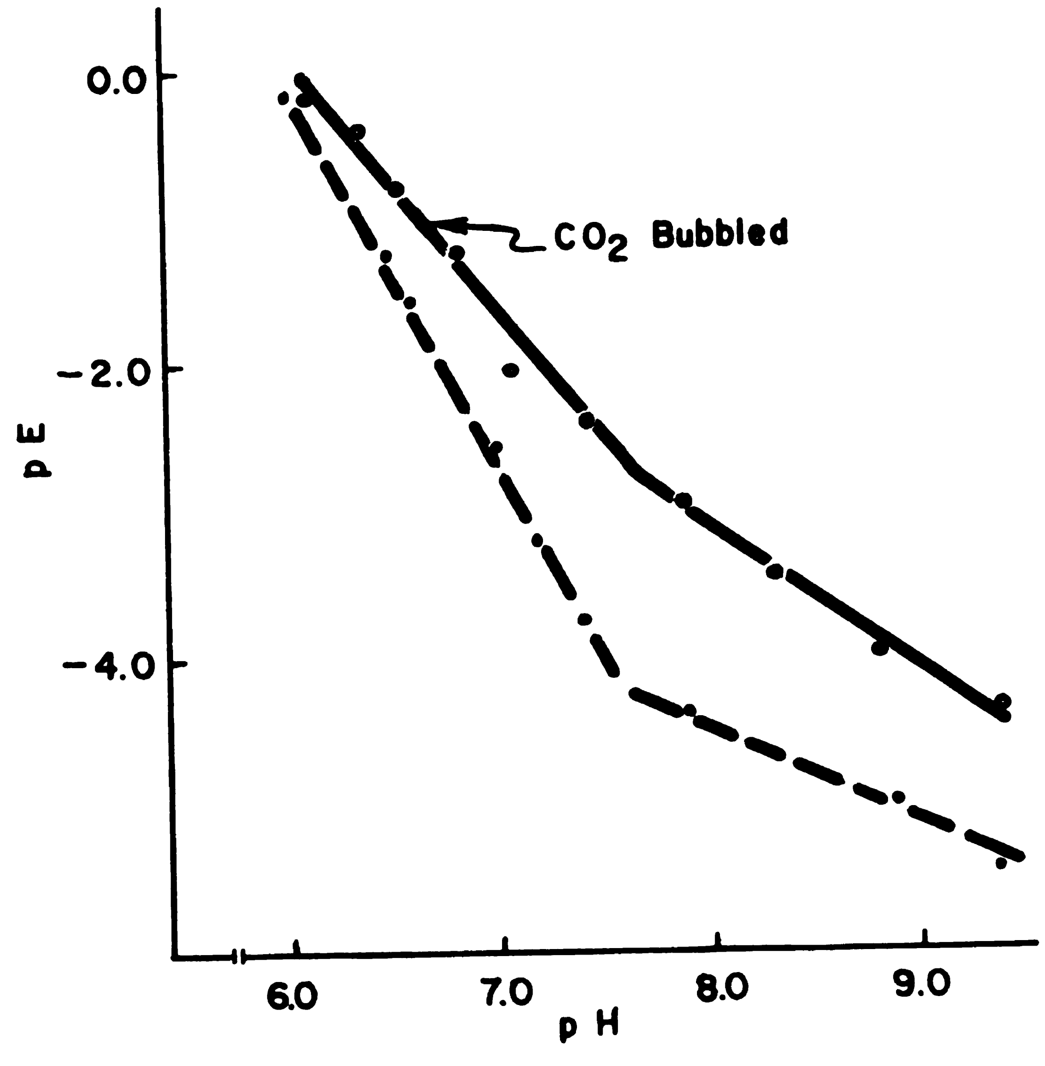
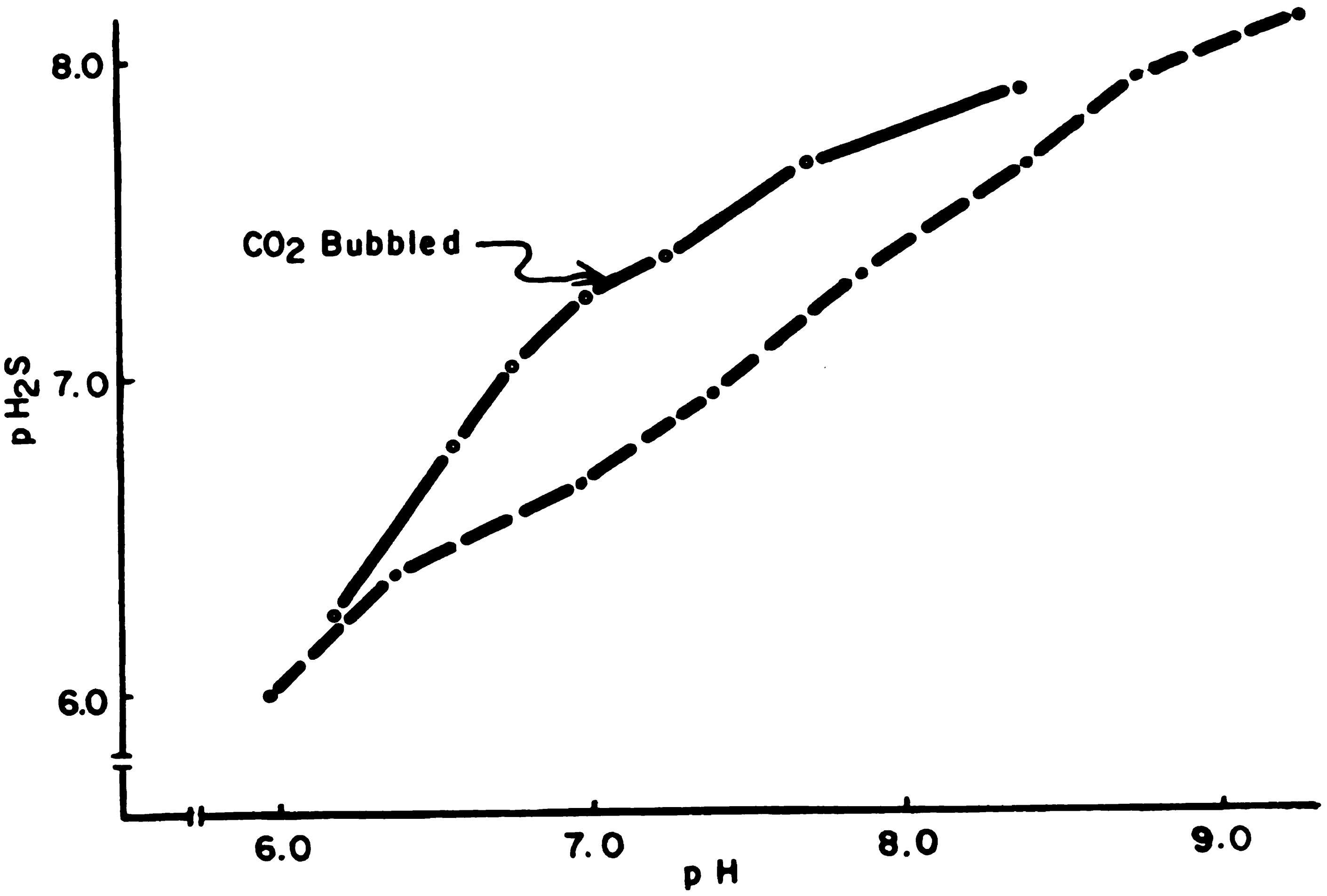


Figure 11. Effect of CO_2 on the pH-pE relationship for the system involving a 1:1 mixture of Fe^{+++} and Fe^{++}.



·Figure 12. Effect of CO_2 on the pH–pH_2S relationships for the system involving a 2:1 mixture of Fe^{+++} and Fe^{++}.

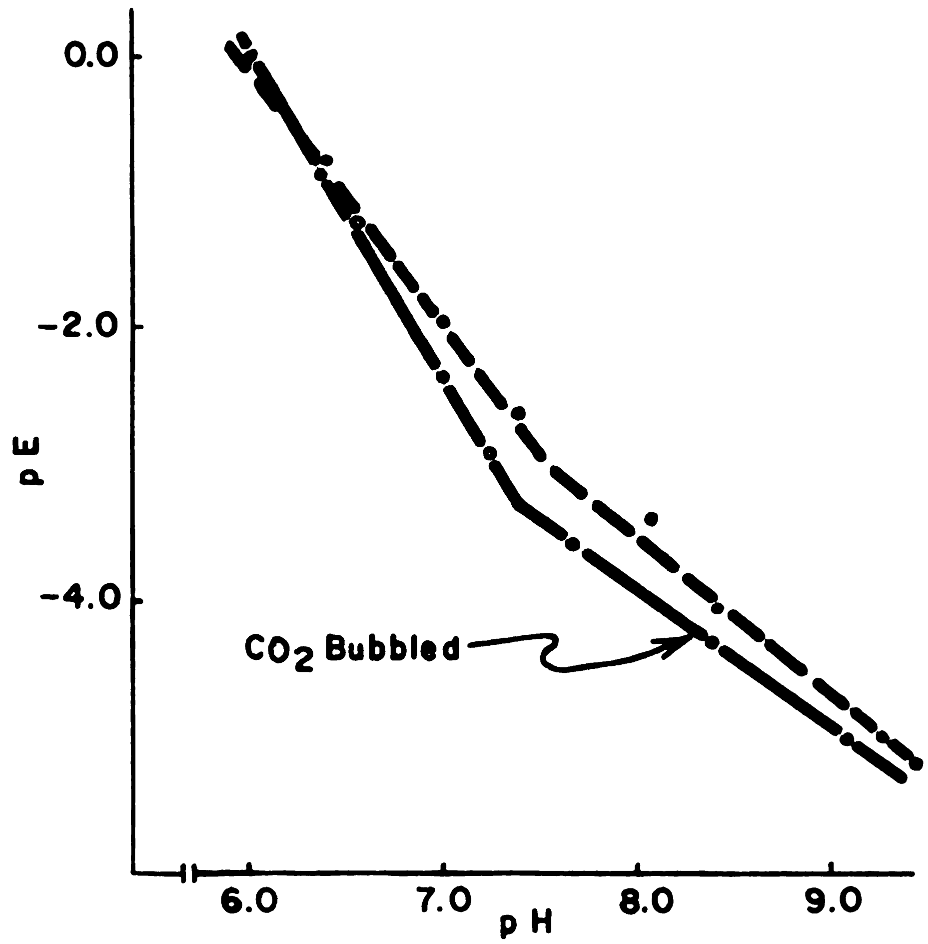


Figure 13. Effect of CO_2 on the pH-pE relationship for the system involving a 2:1 mixture of Fe^{+++} and Fe^{++}.

pH-pE in two soil systems. In soil 2, which was more reduced than soil 1, the pH-pH_2S relationship was more or less similar in pattern to that of Fe systems in the presence of CO_2. While in soil 1, which was not properly reduced, the pH-pH_2S relation somewhat resembled that of a 2:1 mixture of Fe^{3+} and Fe^{++}. The empirical equations for pH-pE in the soil systems were:

Soil 1, acidic system : pE = 8.96 - 1.50 pH . . . . . . (91)

alkaline system : pE = 5.81 - 1.10 pH . . . . . . (92)

Soil 2, acidic system : pE = 14.15 - 2.15 pH . . . . . (93)

alkaline system : pE = 6.88-1.17 pH . . . . . . (94)

From these pH-pE equations it appeared that the Fe compounds in reduced soils under acid conditions are difficult to identify. However, under alkaline conditions, it appeared that the redox couple $Fe(OH)_3$-$Fe_3(OH)_8$ may have been operating, because equations (92) and (94) are more or less close to the theoretical pH-pE equation for the $Fe(OH)_3$-$Fe_3(OH)_8$ couple.

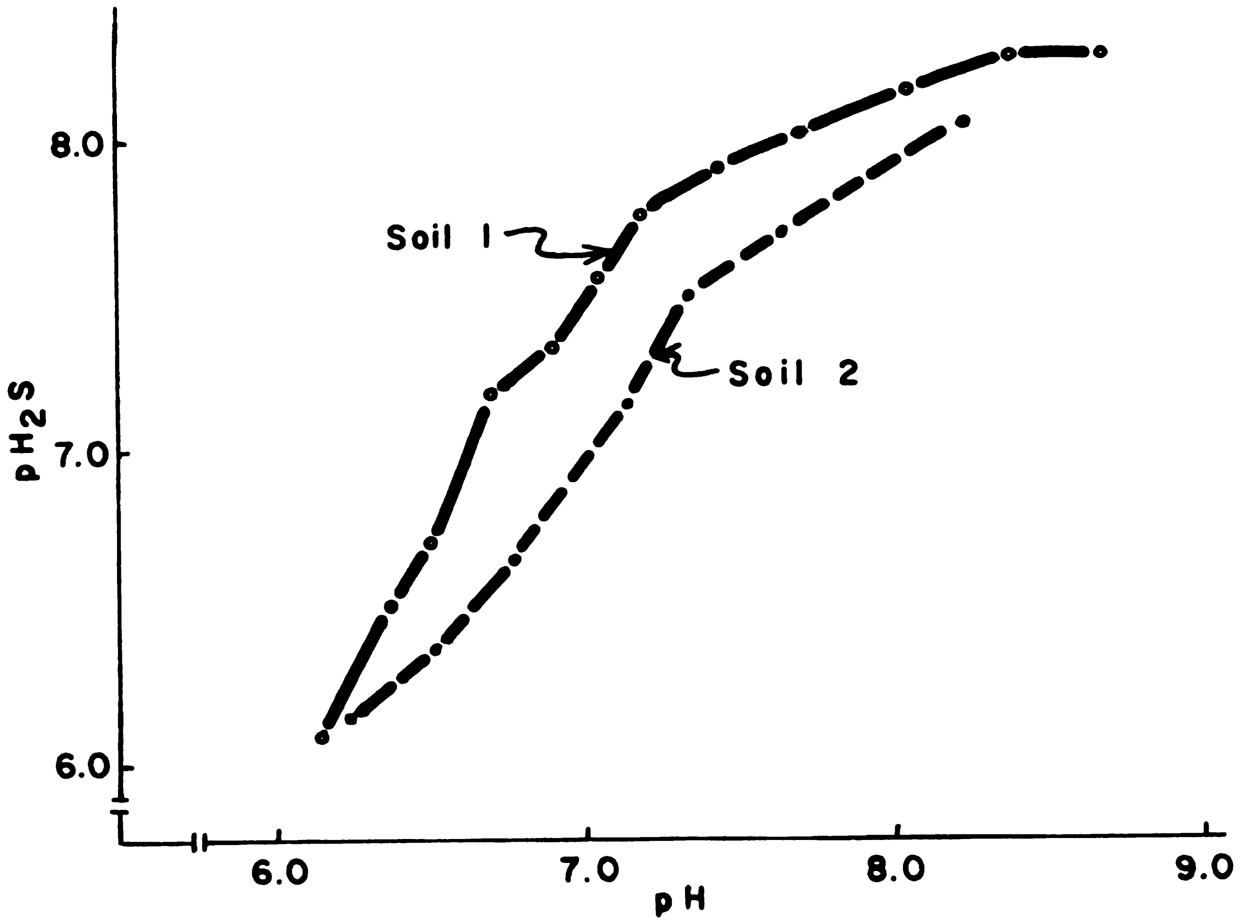


Figure 14. pH-pH_2S relationship for the reduced soil system.

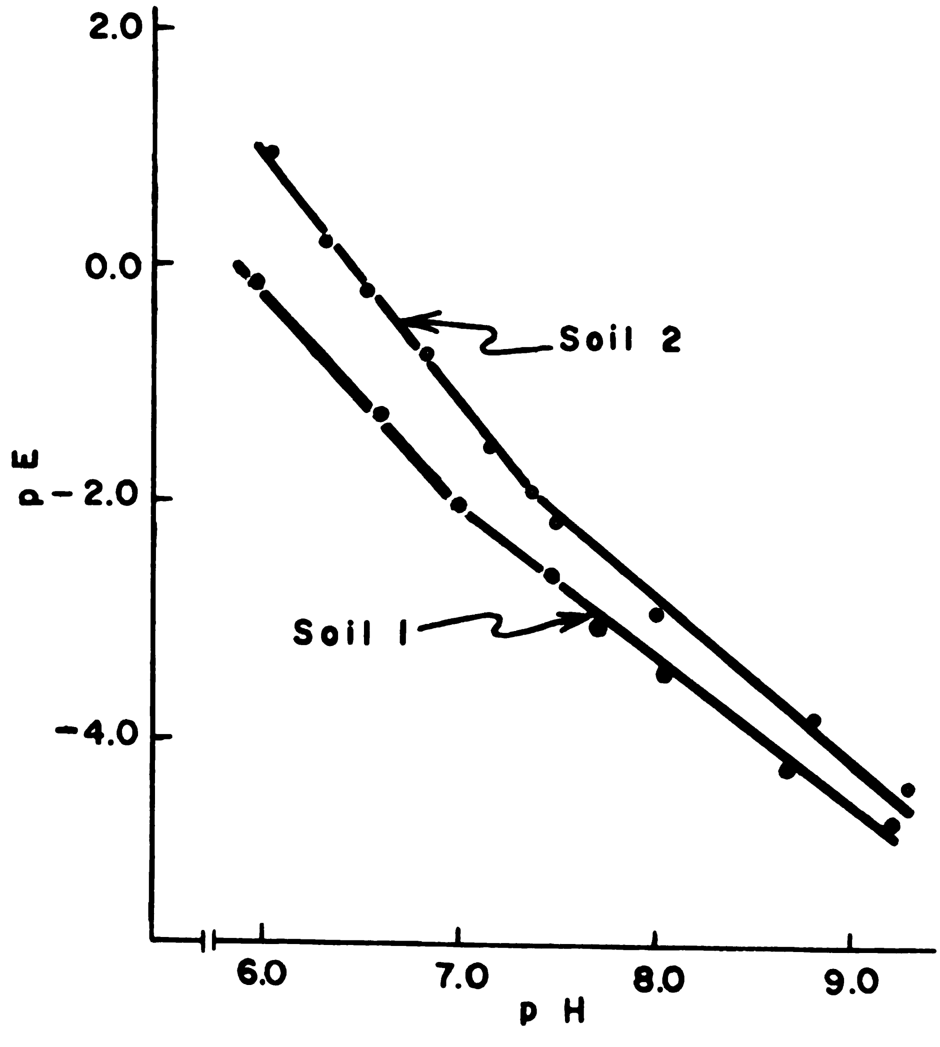


Figure 15. pH-pE relationship for the reduced soil system.

SURVEY OF THE ACTIVITY OF H_2S IN KOREAN PADDY SOILS

A. Objective

From the foregoing experimental findings it is expected that the activity of H_2S in ordinary paddy soils may not exceed the level of 10^{-6} mol/l or 0.034 ppm as H_2S. However this may not always be true in practical soils. Peculiar conditions may exist such as low pH, high organic matter content and excessively high levels of active sulfur; these might allow the accumulation of H_2S in higher concentrations.

The objective of this survey was to obtain some practical information on the quantitative aspects of H_2S in major Korean paddy soils under submerged conditions.

B. Materials and Methods

A group of 194 top soil samples were randomly selected out of 2,000 previously collected from major rice growing areas throughout the country for the study of general fertility status of Korean paddy soils.

A 50g portion of soil was submerged in distilled water in a polyethylene vial. Prior to submergence, soil was amended with 0.5% (w/w) of soluble starch to assure reduction. The vial was covered with a cap to avoid the rapid loss of water. The soils treated in this way were incubated at 30°C for six weeks. The incubated soils were subjected to analysis for pH and sulfide activity. Immediately before the analysis, the solution overlying the soil was gently decanted and the uppermost layer of soil was also removed. The soil remaining in the vial was stirred gently to make a soil slurry. The activity of sulfide and pH were measured in the soil slurries using glass, calomel and sulfide electrodes.

C. Results and Discussion

The activity of H_2S in relation to pH of the soils is depicted in Figure 16. The activity of H_2S ranged from $10^{-5.2}$ to $10^{-7.5}$ mol/l (0.22 to 0.001 ppm) with the average value of $10^{-6.54}$ mol/l (0.009 ppm). The value of 0.22 ppm may be taken as a remarkably high concentration for H_2S, and probably not common in the field soil condition. It is important to consider the pH of the reduced soils in this experiment for the right interpretation of the very high H_2S concentrations that were found. The pH of the soils ranged from 5.3 to 7.0, with an average value of 6.2, which is much lower than is commonly encountered in reduced paddy soils in the field. The lower pH range in these experimental systems may have been due to the unusual treatment that the soils received. The addition of soluble starch at the rate of 0.5% to the soil and the covering of the systems, may have led to unusual accumulations of organic acids and CO_2 which in turn lowered the pH of the soils substantially.

Thus, the data for the activity of H_2S in the present study may not be representative for Korean paddy soils. Nevertheless, the highly significant correlation of pH_2S with pH of the soils, as shown in Figure 16, is of both practical and theoretical interest.

The empirical pH-pH_2S equation is close to the theoretical pH-pH_2S equation in the system $FeCO_3$-FeS.

Empirical : $pH_2S = 1.4\ pH - 2.12$

Theoretical : $pH_2S = 1.5\ pH - 2.85$

The closeness of these two equations suggests that carbon dioxide in association with ferrous iron may determine the activity of H_2S in reduced paddy soils. According to the empirical equation, in the pH range of

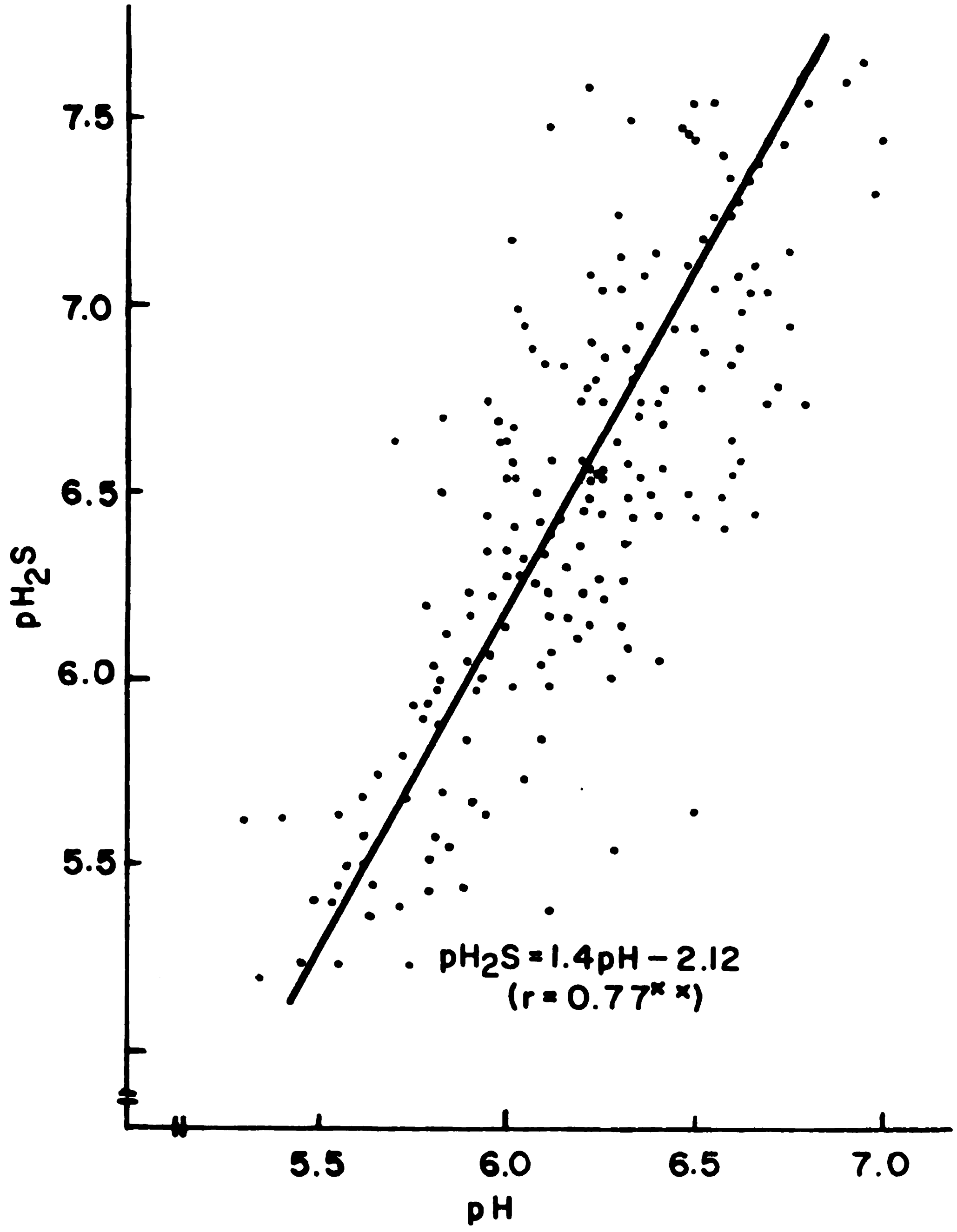


Figure 16. pH-pH$_2$S relation for major Korean paddy soils.

6.0 to 7.0 which is most commonly encountered in reduced paddy soils, the activity of H_2S may fall in the range of $10^{-6.18}$ to $10^{-7.68}$ mol/l or 0.026 to 0.0007 ppm.

SUMMARY AND CONCLUSION

It has been thoroughly documented that H_2S is harmful to rice plants. However, this fact in itself cannot be taken as evidence that H_2S toxicity actually occurs under field conditions. To assess the possibility of its occurrence in the field, one needs quantitative information on just how high the concentration of H_2S must be in soils for toxicity to occur and whether such a concentration of H_2S can be attained in soil systems.

It is generally accepted that an extremely low concentration of H_2S (as low as 0.07 ppm) is enough to be toxic to young rice seedlings. However, some workers maintain that the critical concentration of H_2S for toxicity may be considerably higher (the order of a few parts per million).

The submerged paddy soil is not a simple anoxic system. While it may be anoxic, it is at the same time, a typical anaerobiotic system. Through the anaerobiosis prevailing in the system, oxidized sulfur species are reduced to sulfide. Provided that the system is free from metallic ions, the sulfide produced in such a manner may exist as free H_2S in an acidic condition. The reduced condition and the anaerobiotic processes occurring in submerged soils also favor the reduction of insoluble ferric iron to soluble ferrous iron compounds. Thus, the result of soil reduction is to increase the activity of H_2S in the system, and at the same time to increase the activity of ferrous iron that can suppress the activity of H_2S.

Except in extraordinary cases, paddy soils will contain enough Fe to inactivate the sulfide produced upon reduction. This means that the sulfide in reduced paddy soils exists mainly as sparingly soluble iron sulfide (FeS).

Consequently, the activity of H_2S in the reduced soil systems will be determined by the solubility characteristic of iron sulfide. The relationships among the activities of H_2S, Fe^{++}, and pH in the system involving iron sulfide has been defined as,

$$pH_2S = 2pH - pFe^{++} - K$$

This equation shows that if the activity of Fe^{++} and the pH of a system are known, then the activity of the H_2S in the system can be estimated.

It has been widely accepted that the activity of Fe^{++} in reduced soils is controlled by the solubility of a certain type of iron hydroxide. The chemical characteristics of submerged soils, however, does not allow complete acceptance of this principle. The anaerobiosis prevailing in submerged soils results not only in an increased intensity of reduction, but also gives rise to the extensive accumulation of CO_2. When CO_2 accumulates to levels that are commonly encountered in submerged paddy soils, the CO_2 will definitely influence both the pH and the activity of Fe^{++} in the system. In order to correctly predict the activity of H_2S in submerged soils, knowledge of the activity relationship of Fe^{++} in carbonate systems seems to be essential.

From the theoretical investigation of relationships among pH and the activities of Fe^{++} and H_2S in the system involving Fe^{++}, CO_2, H_2S and H_2O, the following equations were derived:

$$pFe^{++} \triangleq 0.5\ pH + 0.3$$

$$pH_2S = 3/2\ pH - 2.86$$

Experiments with pure $FeCO_3$-H_2CO_3-CO_2 and $FeCO_3$-FeS-H_2O-CO_2-H_2S systems demonstrated the validity of these equations, within the limits of the stability field of $FeCO_3$, that is below pH 7.2. With fifteen moderately acidic alluvial paddy soils, it was found that the pH-pFe^{++} relationships are reasonably close to that of the $FeCO_3$-H_2O-CO_2 system, indicating that the activity of Fe^{++} in the reduced paddy soils is controlled by the $FeCO_3$ system and not by the iron hydroxide systems in such soils.

Investigations on the pH-pH_2S and pH-pE relationships among Fe compounds prepared by alkalizing solutions containing Fe^{3+} and Fe^{++} in varying ratios, and contaminated with FeS, revealed that ferrosoferric hydroxide ($Fe_3(OH)_8$) would not be likely to occur, although heretofore it has been considered to occur commonly in ferruginous reduced paddy soils. It was shown that, in the acid pH range, Fe exists in oxide forms, such as Fe_2O_3, Fe_3O_4 and some intermediates of these, regardless of the ratio in which Fe^{3+} and Fe^{++} are mixed. Only in alkaline systems where the ratio Fe^{++}/Fe^{3+} was 2 or greater was the occurrence of $Fe_3(OH)_8$ possible. In moderately reduced paddy soils, it was shown that the redox potential and the activity of H_2S were controlled by the Fe_2O_3-$FeCO_3$-FeS system in the pH range of 6.0 to 7.0.

The activity of H_2S in all of the Fe systems investigated was found to be less than 10^{-6} mol/l in the pH range of 6.0 to 7.0 commonly found in paddy soils. A survey of the activity of H_2S in major Korean paddy soils disclosed that there is a highly significant negative correlation between the activity of H_2S and pH of the reduced soils. The empirical equation was quite similar to the equation for the system, $FeCO_3$-FeS-H_2O-CO_2-H_2S. From empirical equations, it was predicted that the activities of H_2S at pH 6.0 and 7.0 may be $10^{-6.18}$ and $10^{-7.68}$ mol/l or 0.026 and 0.0007 ppm, respectively.

Following are the significant inferences which can be drawn from the present research.

1. In ordinary submerged paddy soils, the activity of Fe^{++} seems to be determined by the system $FeCO_3$-H_2O-CO_2. In such cases, the pH-pFe^{++}

relationships may be defined as

$$pFe^{++} \hat{=} 0.5\ pH + 0.3$$

2. The dominant redox couples in submerged paddy soils in the pH range 6.0 to 7.0 appears to involve iron oxides rather than iron hydroxides in couples such as Fe_2O_3-Fe^{++} and Fe_3O_4-Fe^{++}.
3. The activity of H_2S in submerged paddy soils can be approximated by using the following equation:

   $$pH_2S = 3/2\ pH - 2.86$$
4. The possibility of the occurrence of H_2S at toxic levels in major Korean paddy soils appears remote.

LITERATURE CITED

Adams, F. 1971. Ionic concentration and activities in soil solutions. Soil Sci. Soc. Amer. Proc. 35:420-426.

Akabori, S., and H. Tamia. 1950. Advances in enzyme chemistry, Japan, Vol. 3, p. 202.

Alexander, M. 1961. Introduction to Soil Microbiology. John Wiley and Sons, Inc. 472 pp.

Allam, A. I., and J. P. Hollis. 1971. Sulfide inhibition of oxidases in rice roots. Phytopathology 62:634-639.

Aoki, M. 1940. On the reduction of nitrate in paddy soils. J. Sci. Soil and Manure, Japan 14:63-76.

Aomine, S. 1962. A review of research on redox potentials of paddy soils in Japan. Soil Sci. 94:6-13.

Araki, M. 1952. The experimental results on the improvement of akiochi soil in Kyoto Prefecture. J. Sci. Soil and Manure, Japan 23:231.

Arden, T. V. 1950. The solubility products of ferrous and ferric hydroxides. J. Chem. Soc. pp. 882-885.

Aristovskaya, T. V., and G. A. Zavarzin. 1971. Biochemistry of iron in soil, p. 385-408. In A. D. McLaren and J. Skujins (ed.) Soil Biochemistry. Vol. 2. Marcel Dekker, Inc., New York.

Asami, T., and K. Kumada. 1959. A new method for determining free iron in paddy soils. Soil and Plant Food 5:141-146.

Asami, T. 1970. Studies on the behavior of free iron in paddy soils. Part 5. Reduction of synthetic hydrated and natural iron oxides. J. Sci. Soil and Manure, Japan 41:56-58

Atkins, J. G. 1958. Rice disease. U.S. Dept. Agr. Farmers' Bull. 2120: 1-14.

Ayotade, K. A. 1972. Studies on hydrogen sulfide, measurement levels and equilibria in solutions of submerged soils. A Terminal Report IRRI, Los Banos, Philippines.

Baas-Becking, L. G. M., I. R. Kaplan, and D. Moore. 1960. Limits of natural environment in terms of pH and oxidation-reduction potentials. J. Geol. 68:243-284.

Baba, I., Y. Takahashi, and I. Iwada. 1952. Studies on the nutrition of rice with reference to Helminthosporium disease (preliminary report). II. The nutrient absorption of rice as affected by the hydrogen sulfide added to culture solution. Crop Sci. Soc. Jap. Proc. 21:98-99.

Baba, I., Y. Takahashi, and I. Iwada. 1953. Studies on the nutrition of rice plant with reference to Helminthosporium leaf spot (preliminary report). IV. Nitrogen metabolism as affected by hydrogen sulfide. Crop Sci. Soc. Jap. Proc. 21:235-236.

Baba, I., and T. Harada. 1954. Physiological diseases of rice plants in Japan. Min. Agr. Forestry, Japan.

Baba, I., Y. Takahashi, I. Iwada, and K. Inada. 1955. Studies on the nutrient of rice plant with reference to the occurrence of the akagare disease. II. Influence of the supply of organic acid and hydrogen sulfide to the soil upon the occurrence of the disease. Crop Sci. Soc. Jap. Proc. 23:273.

Baba, I. 1958. Studies on the nutrition of the rice plant with relation to the occurrence of "Akagare" disease. Crop Sci. Soc. Jap. Proc. 26:190-192.

Baba, I., K. Inada, and K. Tajima. 1965. Mineral nutrition and the occurrence of physiological diseases, p. 182. In Proceedings Symposium on the Mineral Nutrition of the Rice Plant. IRRI. Johns Hopkins Press, Baltimore, Maryland. 494 pp.

Bell, R. G. 1969. Studies on the decomposition of organic matter in flooded soil. Soil Biol. Biochem. 5:659-672.

Berner, R. A. 1963. Electrode studies of hydrogen sulfide in marine sediments. Geochim. et Cosmochim. Acta 27:563-575.

Berner, R. A. 1964. Iron sulfides formed from aqueous solution at low temperature and atmospheric pressure. J. Geol. 72:293-306.

Bloomfield, C. 1953a. A study of podzolization. Part I. The mobilization of iron and aluminum by scots pine needles. J. Soil Sci. 4:5-15.

Bloomfield, C. 1953b. A study of podzolization. Part II. The mobilization of Fe and Al by the leaves and bark of Agathis australia (Kauri). J. Soil Sci. 4:17-23.

Bloomfield, C., and G. Pruden. 1962. Rep. Rothamsted Exp. Sta. for 1962. pp. 75-76.

Bloomfield, C., and G. Pruden. 1967. Rep. Rothamsted Exp. Sta. for 1967. p. 78.

Bloomfield, C. 1969. Sulfate reduction in waterlogged soils. J. Soil Sci. 20:207-222.

Bohn, H. L. 1968. Electromotive forces of inert electrodes in soil suspensions. Soil Sci. Soc. Amer. Proc. 32:211-215.

Bohn, H. L. 1969. The EMF of platinum electrodes in dilute solutions and its relation to soil pH. Soil Sci. Soc. Amer. Proc. 33:639-640.

Bohn, H. L. 1971. Redox potentials. Soil Sci. 112:39-45.

Bostroem, K. 1967. Some pH controlling redox reactions in natural waters, p. 286-311. In Werner Stumm (ed.) Equilibrium Concepts in Natural Water Systems. Adv. Chem. Ser., 67. American Chem. Soc., Washington D. C. 344 pp.

Bradfield, R. 1941. Calcium in the soil. I. Physicochemical relations. Soil Sci. Soc. Amer. Proc. 6:8-15.

Bremner, J. M., S. G. Heintze, P. J. G. Mann, and H. Less. 1946. Metallo-organic complexes in soil. Nature 158:790-791.

Bromfield, S. M. 1954. The reductions of iron oxide by bacteria. J. Soil Sci. 5:129-139.

Brooks, R. R., B. J. Presley, and I. R. Kaplan. 1968. Geochim. Cosmochim. Acta 32:397-414. Cited by Ponnamperuma, F. N. 1972. Chemistry of submerged soils. Adv. in Agr. 24:29-96.

Brown, G. 1953. The occurrence of lepidocrocite in some British soils. J. Soil Sci. 4:220-228.

Brown, G. 1954. Soil morphology and mineralogy. A quantitative study of some gleyed soils from North-West England. J. Soil Sci. 5:145-155.

Buehrer, T. F., W. P. Martin, and R. Q. Parks. 1939. The oxidation-reduction potential of alkaline calcareous soils in relation to puddling and organic matter decomposition. J. Amer. Soc. Agr. 31: 903-914.

Chiu, T. F. 1966. Iron and manganese absorption by rice plants. Soil and Fert., Taiwan 1966:1-6.

Cho, D. Y. 1970. The influence of soil temperature regimes on the chemical kinetics of flooded soils and the growth of rice. M.S. Thesis. Univ. of Philippines, Los Banos, Philippines.

Cho, D. Y., and I. K. Chung. 1971. Studies on the dynamics of growth inhibiting substances in the reduced paddy soil. Res. Rep. Inst. Plant Environ. Korea for 1971. pp. 1024-1076.

Cho, D. Y., M. K. Lee, and Y. T. Oh. 1972. Study on the relationship between the chemical characteristics and the nutrient release of waterlogged soil. Res. Rep. Inst. Plant Environ. Korea for 1972. pp. 849-861.

Clark, J. S. 1964. An examination of the pH of calcareous soils. Soil Sci. 98:145-151.

Cole, C. V. 1957. Hydrogen and calcium relationship of calcareous soils. Soil Sci. 83:141-150.

Connel, W. E., and W. H. Patrick, Jr. 1969. Reduction of sulfate to sulfide in waterlogged soil. Soil Sci. Soc. Amer. Proc. 33:712-715.

Coperland, O. L., Jr. 1957. A study of the influence of moisture and compaction on soil oxidation-reduction potentials. Soil Sci. Soc. Amer. Proc. 21:269-271.

Delwiche, C. C. 1967. Energy relationships in soil biochemistry, p. 173-193. In A. D. McLaren and G. H. Peterson (ed.) Soil Biochemistry. Marcel Dekker, Inc., New York.

Engler, R. M. 1972. Oxidation-reduction reactions of sulfate and sulfide in flooded and nonflooded soil. Ph.D. Thesis. Louisiana State Univ., Baton Rouge, Louisiana.

Frear, G. L. and J. Johnston. 1929. The solubility of calcium carbonate (calcite) in certain aqueous solution at 25°C. J. Amer. Chem. Soc- 51:2082-2093.

Freney, J. R. 1967. Sulfur-containing organics, p. 229-259. In A. D. McLaren and G. H. Peterson (ed.) Soil Biochemistry. Marcel Dekker, Inc., New York.

Garrels, R. M., and C. L. Christ. 1965. Solutions, minerals and equilibria. Tokyo, Japan. pp. 172-266.

Gillespie, L. J. 1920. Reduction potentials of bacterial cultures and of waterlogged soils. Soil Sci. 9:199-216.

Gotoh, S., and K. Yamashita. 1966. Oxidation-reduction potential of a paddy soil in situ with special reference to the production of ferrous iron, manganous manganese and sulfide. Soil Sci. and Plant Nutr. 12:230-238.

Gotoh, S., and W. H. Patrick, Jr. 1972. Transformation of manganese in a waterlogged soil as affected by redox potential and pH. Soil Sci. Soc. Amer. Proc. 36:738-742.

Halvarson, H. O. 1931. Studies on the transformation of iron in nature. III. The effect of CO_2 on the equilibrium in iron solutions. Soil Sci. 32:141-165.

Han, K. W. 1973. Sulfur availability to rice plants and its transformations in rice soil and rhizosphere. M.S. Thesis. Univ. of Philippines, Los Banos, Philippines.

Hashimoto, H., D. Koda, and S. Mitsui. 1948. Effect of application of silica and bases on degraded paddy soils. J. Sci. Soil and Manure, Japan 19:61.

Hem, J. D. 1960a. Restraints on dissolved ferrous iron imposed by bicarbonate, redox potential, and pH. U.S. Geol. Surv. Water-Supply Pap. 1450-B.

Hem, J. D. 1960b. Some chemical relationships among sulfur species and dissolved iron. U.S. Geol. Surv. Water-Supply Pap. 1459-C.

Hollis, J. P. 1967. Toxicant diseases of rice. Louisiana Agr. Exp. Sta. Bull. 614.

Hong, C. W. 1972. The fertility status of Korean soils. In ASPAC Technical Bull. No. 10, Part 2:56-84.

Inada, K. 1962. Mineral nutrition and the occurrence of physiological diseases, p. 173-195. In Proceedings Symposium on the Mineral Nutrition of the Rice Plant. IRRI. Johns Hopkins Press, Baltimore, Maryland. 494 pp.

Inoue, H. 1953. Report of the experimental results on a kind of straight head. Part I. Hyogo Pref. Agr. Exp. Sta.

International Rice Research Institute. 1964. Annual report for 1963. Los Banos, Philippines. 65 pp.

International Rice Research Institute. 1966. Annual report for 1965. Los Banos, Philippines. pp. 106-117.

International Rice Research Institute. 1972. Annual report for 1971. Los Banos, Philippines. 205 pp.

International Rice Research Institute. 1973. Annual report for 1972. Los Banos, Philippines. pp. 189-205.

Ito, M. 1948. Study on the characteristics of soil materials used for the improvement of degraded soils. J. Sci. Soil and Manure, Japan 19:45-46.

Jackson, M. L. 1958. Soil Chemical Analysis. Prentice Hall, Inc., New Jersey. 498 pp.

Jeffery, J. W. O. 1961. Defining the state of reduction of a paddy soil. J. Soil Sci. 12:172-179.

Jones, H. T., and J. S. Wilcox. 1929. Studies in soil genetics. J. Soc. Chem. Ind., London. 48:304-308.

Joffe, J. S. 1935. Soil profile studies. VII. The glei process. Soil Sci. 31:391-401.

Kamoshita, Y., and Y. Iwasa. 1959. On the rusty mottles in paddy field soils. J. Sci. Soil and Manure, Japan 30:185-188.

Kamura, T., and Y. Takai. 1961. The mechanisms of microbial reduction of ferric iron in paddy soil. J. Sci. Soil and Manure, Japan 32:135-138.

Kamura, T., Y. Takai, and K. Ishikawa. 1963. Microbial reduction mechanism of ferric iron in paddy soils. Soil Sci. and Plant Nutr. 9:171-175.

Kataoka, I., and T. Kitamura. 1959. Studies on brown gel (hydrated ferric oxide). III. The relationship between drying and aging of the gel. J. Sci. Soil and Manure, Japan 31:18-22.

Katyal, J. C. 1972. A study of zinc equilibrium in flooded soils and amelioration of zinc deficient soils of Agusan Del Norte. Terminal Rep. for Fellowship. IRRI, Los Banos, Philippines.

Keller, R. N., and R. W. Parry. 1956. Modern developments: The electron pair bond and structure of coordination compounds, p. 157-219. In J. C. Bailar and D. H. Busch (ed.) The Chemistry of Coordination Compounds. Reinhold Publishing Corporation, New York.

Killand, J. 1939. Individual activity coefficients of ions in aqueous solutions. J. Amer. Chem. Soc. 59:1675-1678.

Kohnke, H. 1934. Some factors affecting the oxidation reduction potentials of soils. Ph.D. Thesis. Ohio State University.

Kojima, M., and K. Kawaguchi. 1968. Composition of iron mottles in paddy soils. J. Sci. Soil and Manure, Japan 31:349-353.

Krauskopf, K. B. 1967. Introduction to Geochemistry. MacGraw-Hill Book Co. New York. 721 pp.

Kumada, K. 1948. Studies on the soil of rhizosphere of rice plant. Part I. Micro-structure of rhizosphere soils and the oxidative power of rice roots. J. Sci. Soil and Manure, Japan 19:119-124.

Kumada, K. 1950. Study on the chemistry of paddy soils (15). The effect of the application of iron oxide on the decomposition of organic matter. J. Sci. Soil and Manure, Japan 21:151-152.

Kyuma, I., and K. Kawaguchi. 1966. The redox potential and the equilibrium of ferrous iron in soil solutions of paddy soils. J. Sci. Soil and Manure, Japan 37:354.

Kyuma, I. 1967. pH and Eh of the paddy soil solutions. J. Sci. Soil and Manure, Japan 38:99-100.

Langelier, W. F. 1936. The analytical control of anticorrosion water treatment. J. Amer. Water Works Assoc. 25:1500-1521.

Latimer, W. M. 1952. The oxidation states of the elements and their potentials in aqueous solutions. Prentice Hall, Inc., Englewood Cliffs, New Jersey. 392 pp.

Lee, H. C. 1956. Studies on Tung-Shan paddy soils. Ilan Hsien. Taiwan Agr. Res. Inst. Bull. 15:17.

Lee, M. K. 1973. Study on the release of available nutrients in the reduced paddy soils. Inst. Agr. Sci. Res. Rep. for 1973. pp. 366-374.

Lehman, D. S. 1963. Some principles of chelation chemistry. Soil Sci. Soc. Amer. Proc. 27:167-178.

Martell, A. E., and M. Calvin. 1962. Chemistry of the metal compounds. Prentice Hall, Inc. Englewood Cliffs, New Jersey. 191 pp.

Mitsui, S., A. Aso, and K. Kumazawa. 1951. Dynamics studies on the nutrients uptake by crop plants. Part I. The nutrients uptake of rice root as influenced by H_2S. J. Sci. Soil and Manure, Japan 22:46-52.

Mitsui, S., K. Kumazawa, and N. Mukai. 1959. Dynamic studies on the nutrient uptake by crop plants. Part 22. The growth of rice plants on poorly drained soil as affected by the accumulation of volatile acids (C). J. Sci. Soil and Manure, Japan 30:345-348.

Moeller, T. 1963. Inorganic chemistry, an advanced textbook. John Wiley and Sons, Inc.,New York. 966 pp.

Mori, T. 1954. Studies on ecological characteristics of rice root. 1. Effect of hydrogen sulfide on root growth of rice plant. Tohoku Univ. Inst. Agr. Res. Bull. 6:1-13.

Morris, J. C., and W. Stumm. 1967. Redox equilibria and measurements of potentials in the aquatic environment, pp. 270-285. In Werner Stumm (ed.) Equilibrium Concepts in Natural Water Systems. Adv. Chem. Ser., 67. American Chem. Soc., Washington D. C. 344 pp.

Mortensen, J. L. 1963. Complexing of metals by soil organic matter. Soil Sci. Soc. Amer. Proc. 27:177-186.

Mortimer, C. E. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 30:280-329.

Motomura, S., T. Akiyama, and K. Yamanaka. 1961. Effect of the addition of organic matter on the metabolism of soils under waterlogged condition. J. Sci. Soil and Manure, Japan 32:605-612.

Motomura, S., K. Yamanaka. 1962. Study on the gleyzation of soils. Part 3. Relationship between the formation of ferrous iron and nitrogen metabolism of soils. J. Sci. Soil and Manure, Japan 33:392-396.

Nakayama, F. S. 1971. Problems associated with the determination and application of the solubility product constants. Soil Sci. Soc. Amer. Proc. 35:442-445.

Nhung, M. M., and F. N. Ponnamperuma. 1966. Effects of calcium carbonate, manganese dioxide, ferric hydroxide, and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulfate soil. Soil Sci. 102:29-41.

Oades, J. M. 1963. The nature and distribution of iron compounds in soils. Soil and Fert. 26:69-80.

Okajima, H., and S. Takagi. 1953a. Physiological behavior of hydrogen sulfide in rice plant. Part I. Effect of hydrogen sulfide on the absorption of nutrient. Tohoku Univ. Inst. Agr. Res. Bull. 5:139-146.

Okajima, H., and S. Takagi. 1953b. Physiological behavior of hydrogen sulfide in rice plant. Part II. Effect of hydrogen sulfide on absorption of nutrients in rice plant. Tohoku Univ. Inst. Agr. Res. Bull. 5:165-176.

Okajima, H., and S. Takagi. 1955. Physiological behavior of hydrogen sulfide in rice plant. Part V. Effect of hydrogen sulfide on respiration of rice roots. J. Sci. Soil and Manure, Japan 26:37-42.

Olomu, M. C., G. J. Racz, and C. M. Cho. 1973. Effect of flooding on the Eh, pH and concentrations of Fe and Mn in several Manitoba soils. Soil Sci. Soc. Amer. Proc. 37:220-224.

Olsen, S. R., and F. S. Watanabe. 1959. Solubility of calcium carbonate in calcareous soils. Soil Sci. 88:123-129.

Osugi, S., and K. Kawaguchi. 1938. Study on the damages induced by the application of ammonium sulfate to paddy soils. J. Sci. Soil and Manure, Japan 12:453-462.

Ota, Y., and N. Yamada. 1960. Physiological effect of iron on rice plants. II. Effect of iron in relation to soil reduction. Proc. Crop Sci. Soc., Japan 28:367-370.

Park, N. J., Y. S. Park, and Y. S. Kim. 1971. Effect of lime on the growth of rice and the changes in pH, Eh, Fe^{++}, and Al^{+++} in an acid sulfate soil. J. Kor. Soc. Soil Sci. Fert. 4:167-175.

Park, N. J. 1971. Natural chelates as Fe fertilizer. Ph.D. Thesis. Colorado State Univ., Fort Collins, Colorado.

Park, Y. D., Y. S. Kim, and M. K. Kim. 1964. Study on the inorganic components of rice leaves affected by Helminthosporium disease. J. Kor. Agr. Chem. 5:49-51.

Park, Y. D. 1967. Study on the nutrient absorption of rice plant grown on akiochi soil. Res. Rep. Off. Rur. Dev., Korea 10:23-35.

Park, Y. D., and Y. S. Kim. 1971. Effect of silica on rice in akiochi soil. J. Kor. Soc. Soil Sci. Fert. 4:1-11.

Park, Y. S. 1969. A study on physico-chemical properties and dynamic changes of paddy soils under waterlogged condition. Res. Rep. Off. Rur. Dev., Korea 12:1-18.

Patrick, W. M., Jr. 1960. Nitrate reduction rates in a submerged soil as affected by redox potential. Trans. Int. Congr. Soil Sci. 7th (Madison, Wis.) 2:494-500.

Patrick, W. M., Jr., and I. C. Mahapatra. 1968. Transformations and availability of nitrogen and phosphorus in waterlogged soils. Adv. Agron. 20:323-359.

Pitts, R. G. 1971. Exploration in the chemistry and microbiology of Louisiana rice plant-soil relations. Ph.D. Thesis. Louisiana State Univ., Baton Rouge, Louisiana.

Pitts, G., A. I. Allam, and J. P. Hollis. 1972a. Beggiatoa; Occurrence in the rice rhizosphere. Science 178:990-992.

Pitts, G., A. I. Allam, and J. P. Hollis. 1972b. Aqueous iron-sulfur systems in rice field soils of Louisiana. Plant and Soil 36:251-260.

Ponnamperuma, F. N. 1955. The chemistry of submerged soils in relation to the growth and yield of rice. Ph.D. Thesis. Cornell Univ., Ithaca, New York.

Ponnamperuma, F. N. 1958. Lime as a remedy for physiological disease of rice associated with excess iron. I.R.C. Newsletter 1(1):10-13.

Ponnamperuma, F. N. 1965. Dynamic aspects of flooded soils and nutrition of the rice plant, p. 295-328. In Proceedings Symposium on the Mineral Nutrition of the Rice Plant. IRRI. Johns Hopkins Press, Baltimore, Maryland. 494 pp.

Ponnamperuma, F. N., E. Martinez, and T. Loy. 1965. Influence of redox potential and partial pressure of carbon dioxide on pH values and the suspension effect of flooded soils. Soil Sci. 101:421-431.

Ponnamperuma, F. N. 1966. A theoretical study of aqueous carbonates equilibria. Soil Sci. 103:90-100.

Ponnamperuma, F. N., E. M. Tianco, and T. A. Loy. 1966. Ionic strengths of the solutions of flooded soils and other natural aqueous solutions from specific conductances. Soil Sci. 102:408-413.

Ponnamperuma, F. N., E. M. Tianco, and T. Loy. 1967. Redox equilibria in flooded soils: I. The iron hydroxide systems. Soil Sci. 103: 374-382.

Ponnamperuma, F. N., T. Loy, and E. M. Tianco. 1968. Redox equilibria in flooded soils: II. The manganese systems. Soil Sci. 108:48-57.

Ponnamperuma, F. N., R. U. Castro, and C. M. Valencia. 1969. Experimental study of the influence of the partial pressure of carbon dioxide on the pH values of aqueous systems. Soil Sci. Soc. Amer. Proc. 33: 239-241.

Ponnamperuma, F. N. 1972a. The chemistry of submerged soils. Adv. Agron. 24:29-95.

Ponnamperuma, F. N. 1972b. Oxidation reduction reactions. In J. Bremmer and G. Chester (ed.) Soil Chemistry. Marcel Dekker, New York. (In press).

Postgate, J. R. 1959. Sulfate reduction by bacteria. Ann. Rev. Microbiol. 13:505-520.

Puri, A. N., and A. Sarup. 1938. Oxidation reduction potentials in soils. Soil Sci. 46:323-329.

Rich, C. I. 1956. Manganese contents of peanut leaves as related to soil factors. Soil Sci. 82:353-363.

Roberts, J. L. 1947. Reduction of ferric hydroxide by strains of *Bacillus polymixa*. Soil Sci. 63:135-140.

Rosenquist, I. Th. 1970. Formation of vivanite in holocene clay sediments. Lithos 3:327-334.

Saheki, H., H. D. Kamoto, and K. Fujii. 1952. Effectiveness of a by-product iron powder. J. Sci. Soil and Manure, Japan 19:61-62.

Saito, B. 1954. Investigations on controlling of the so-called akiochi of the paddy rice plant found in Kyushu. II. The effect of free carbon dioxide on the uptake of nutrients by paddy rice plant. Kyushu Agr. Exp. Sta. Bull. 2:283-293.

Sato, I., and I. Yamane. 1959. The role of soil organic matter in the evolution of free hydrogen sulfide in flooded soil. Tohoku Univ. Inst. Agr. Res. Bull. 11:145-157.

Schindler, P. W. 1967. Heterogeneous equilibria involving oxides, hydroxides, carbonates, and hydroxide carbonates, p. 196-221. *In* Werner Stumm (ed.) Equilibrium Concepts in Natural Water Systems. Adv. Chem. Ser., 67. American Chem. Soc., Washington D. C. 344 pp.

Shiga, H. 1962. Studies on behavior of hydrogen sulfide in waterlogged soils. Unpublished mimeograph.

Shioiri, M. 1943. Soil chemistry of rice fields. Agron. Conf. of Japan 1-63.

Shioiri, M., and H. Yokoi. 1949. The leaching mechanism of iron sulfides. J. Sci. Soil and Manure, Japan 20:157-161.

Shioiri, M., and M. Yoshida. 1951. Study on the behavior of manganese in paddy soil. J. Sci. Soil and Manure, Japan 22:53-56.

Schollenberger, C. J. 1928. Manganese as an active base in the soil. Soil Sci. 25:357-358

Sillen, L. G. 1967. Master variables and activity scales, p. 45-56. *In* Werner Stumm (ed.) Equilibrium Concepts in Natural Water Systems. Adv. Chem. Ser., 67. American Chem. Soc., Washington D. C. 344 pp.

Simmons, C. F. 1939. The effect of carbon dioxide pressure upon equilibrium of the systems hydrogen colloidal clay-H_2O-$CaCO_3$. J. Amer. Soc. Agron. 31:638-648

Starkey, R. L., and H. O. Halvarson. 1927. Studies on the transformation of iron in nature. II. Concerning the importance of microorganisms in the solution and precipitation of iron. Soil Sci. 24:381-401.

Starkey, R. L., and K. M. Wight. 1945. Anaerobic corrosion of iron in soil. Published by the American Gas Association. New York.

Starkey, R. L. 1950. Relations of microorganisms to transformation of sulfur in soils. Soil Sci. 70:55-65.

Starkey, R. L. 1966. Oxidation and reduction of sulfur compounds in soils. Soil Sci. 101:297-306.

Subrahmanyan, V. 1927. Biochemistry of waterlogged soils. III. Decomposition of carbohydrates with special reference to formation of organic acids. J. Agr. Res. 19:627-648.

Suzuke, S., and M. Maeda. 1948. Review on the prevention of akiochi of rice. J. Sci. Soil and Manure, Japan 19:91-92.

Suzuke, S., and K. Honya. 1950. Study on the reduction of submerged soils. Part 2. Development of oxidized and reduced layers. J. Sci. Soil and Manure, Japan 21:59-60.

Takahashi, J. 1961. Physiological disease of rice in Taiwan. Soils and Fert., Taiwan 1961:10-14.

Takai, Y., T. Koyama, and T. Kamura. 1956. Microbial metabolism in reduction process of paddy soils. Part I. Influence of anaerobic incubation on the composition of soil gases. Soil and Plant Food 2 (2):63-66.

Takai, Y., T. Koyama, and T. Kamura. 1957. Microbial metabolism in reduction process of paddy soils. Part 4. On the development of reduction state in different soils (2). Agr. Chem., Japan 31: 215-220.

Takai, Y., T. Koyama, and T. Kamura. 1963. Microbial metabolism in reduction process of paddy soils. Part 2. Effect of iron and organic matter on the reduction process. Soil Sci. and Plant Nutr. 9:176-180.

Takijima, Y. 1963. Studies on behavior of the growth inhibiting substances in paddy soils with special reference to the occurrence of root damage in the peaty paddy fields. Nat. Inst. Agr. Sci. Bull. Ser. B. 13:117-252.

Tanaka, A., R. P. Mullerigawa, and T. Yasu. 1968. Possibility of hydrogen sulfide induced iron toxicity of rice plant. Soil Sci. and Plant Nutr. 14:1-6.

Ueda, K., and S. Kimura. 1959. Studies on the degraded paddy soils (5). The effect of silica and magnesium. J. Sci. Soil and Manure, Japan 30:154-156.

Ueda, K., and Yamaoka. 1959. Studies on the degraded paddy soils (6). Study on the occurrence of akiochi in connection with the insufficiency of silica. J. Sci. Soil and Manure, Japan 30:371-373.

Vamos, R. 1958. H_2S, the cause of bruzone disease of rice. Soil Plant Food 3:37-40.

Vamos, R. 1959. "Bruzone" disease of rice in Hungary. Plant and Soil 11:65-71.

Vamos, R. 1964. The release of hydrogen sulfide iron mud. J. Soil Sci. 5:103-109.

Wallace, A. 1962. Metal chelation and mechanisms of metal function in biological systems, pp. 3-14. In Arthur Wallace (ed.) Decade of Synthetic Chelating Aqents in Inorganic Plant Nutrition. Arthur Wallace, 2278 Parnell Avenue, Los Angeles 64, California.

Whitney, R. S., and R. Gardner. 1943. The effect of carbon dioxide on soil reaction. Soil Sci. 55:127-141.

Willis, L. G. 1932. Oxidation-reduction potentials and the hydrogen ion concentration of a soil. J. Agr. Res. 45:571-575.

Wu, M. M. H., C. S. Wu, M. H. Chiang, and S. F. Chou. 1972. Microbial investigations on the suffocation disesae of rice in Taiwan. Plant and Soil 37:329-344.

Yamaguchi, H., K. Shiratori, and A. Koizumi. 1957. Researches on the technical improvement of rice culture on ill-drained fields. IV-1. Chemical characteristics of akagare paddy soils and classification of them with reference to the occurrence of the so-called akagare. Proc. Crop Sci. Soc., Japan 26:3-4.

Yamane, I. 1958. Metabolism in muck paddy soil. 2. Determination of decomposable organic matter. Soil and Plant Food 4:25-31.

Yamane, I., and K. Sato. 1961a. Metabolism in muck paddy soil. Part 3. Role of organic matter in the evaluation of free hydrogen sulfide in waterlogged soil. Tohoku Univ. Res. Inst. Sci. Rep. Ser. D. 12:1-10.

Yamane, I., and K. Sato. 1961b. Effect of temperature on the formation of gases and ammonium nitrogen in the waterlogged soils. Tohoku Univ. Res. Inst. Sci. Rep. Ser. D. 12:1-10.

Yamane, I. 1967. Some problems in rice soil. Rep. Inst. Agr. Res., Tohoku Univ. 18:87-108.

Yamane, I., and K. Sato. 1968. Initial rapid drop of oxidation-reduction potential in submerged air dried soils. Soil Sci. and Plant Nutr. 14: 68-72.

Yamane, I. 1969. Reduction of nitrate and sulfate in submerged soils with special reference to redox potential and water-soluble sugar content of soils. Soil Sci. and Plant Nutr. 15:139-148.

Yamane, I. 1970. Eh-pH diagrams of iron systems in relation to flooded soils. Rept. Inst. Agr. Res. Tohoku Univ. 21:39-63.

Yamane, I., and K. Sato. 1970. Plant and soil in a lowland rice field added with forage residues. Rep. Inst. Agri. Res. Tohoku Univ. 21: 79-107.

Yoshida, S. 1971. Nutritional disorder of rice in Asia ASPAC Ext. Bull. 4.

Yuan, W. L., and F. N. Ponnamperuma. 1966. Chemical retardation of flooded soils and the growth of rice. Plant Soil 25:347-360.

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