
REDOX POTENTIAL—WITH SPECIAL REFERENCE TO RICE CULTURE

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THERE are numerous reactions in the inorganic and in the organic world which are characterised by the addition of oxygen or hydrogen. The resulting action is either an oxidation reaction or a reduction reaction. One of the classic reductive processes in the organic world is the production of carbohydrates by addition of hydrogen (released from the photolysis reaction) to carbon-dioxide. The reverse process of respiration is an oxidative process. In the inorganic field the spontaneous combination of hydrogen and oxygen is an example of oxidation or reduction. The conversion of ferric ion to ferrous ion in submerged paddy soils is a dominating reduction reaction in the chemical environs of the soil. The only physico-chemical property that serves to differentiate a well drained soil from a submerged soil is its redox potential*. There are many studies of redox potentials in soils, lake muds and waters, bacterial cultures and sewage. Their practical significance is thus described by Pearsall and Mortimer (1) "In the measurement of potential we have a method of showing whether a soil or a natural system is capable of oxidation or otherwise, under conditions where direct oxygen measurements are inconvenient or impracticable. Further, in many cases it is probable that the oxidation reduction potential, i.e., the value which indicates the general level of oxidation or reduction of a system, is a factor of greater biological significance than oxygen concentration alone".

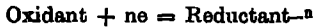
It is proposed in this paper to consider oxidation-reduction under the following headings:—(a) Theory, (b) Oxidation and reduction in pedological processes, (c) Ecology of plant life and ecology of micro-organisms of the soil, (d) Oxidation-reduction systems in soils, (e) Factors influencing the oxidation-reduction potentials of soils, (f) Influence of low oxidation-reduction potential on submerged rice soils and on the rice plant, (g) Measurement of oxidation-reduction potential.

(a) Theory

Oxidation is characterised by the emission of electrons and reduction by the absorption of electrons. Thus oxidation-reduction is a conjugate process.

* Oxidation-reduction potential and redox potential are used inter changeably.

This suggests that the oxidation-reduction power of a system should be measurable by the potentiometric method. It is a quantitative measure of the electron pressure. The degree of this potential can be measured if an inert electrode such as platinum or gold is placed in the system and this half cell set against a half cell consisting of a normal hydrogen or a calomel electrode. Thermodynamically it can be shown that



Modification of the Nernst equation by Peters gives the expression

$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{Oxidant})}{(\text{Reductant})}$$

where E_h is the redox potential relative to the normal hydrogen electrode taken as zero and E_o is a characteristic of the system and equal to E_h when (Oxidant)/(Reductant) is unity. Other symbols have the customary significance. Thus redox potential measures the ratio of oxidant to reductant and is therefore a measure of the intensity of oxidation or reduction.

When two redox systems are mixed a redistribution of electrons takes place among the components which brings the potentials of the two systems to a common value. The final potential is determined by the system which is present in excess. This is illustrated by the numerical example given by Michealis (?) of the interaction between the ferric-ferrous system and the methylene blue-leuco-methylene blue system. He there shows that if the ferric-ferrous system is present in excess practically all the leuco-methylene blue is oxidised without a marked deviation from the potential of the ferric-ferrous system. On the other hand if the methylene blue-leuco-methylene blue system is present in excess practically all the ferric iron may be reduced without changing appreciably the potential of the methylene blue-leuco-methylene blue system. This result is of great importance in interpreting redox potentials of soils which contain many mixed systems.

A property of equal importance, specially in the measurement of redox potentials of soils, is the resistance to change or "poise" of a redox system. Lack of poise is the cause of the electrode drift, the electrode lags, and the failure to get reproducible readings so often referred to in the literature.

An expression for the poise of a system can be derived mathematically from the equation for the redox potential of a system : (3)

$$E = E_o + \frac{RT}{nF} \ln \frac{x}{A-x}$$

in which x = activity of oxidant

A = activity of (oxidant + reductant)

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The increase in redox potential with a small increase in the activity (concentration) of the oxidised phase is given by :

$$\frac{dE}{dx} = \frac{RT}{nF} \cdot \frac{A}{x(A-x)}$$

The reciprocal of $\frac{dE}{dx}$ may be taken as a measure of the poise of the system and is given by the expression :

$$\frac{nF}{RT} \cdot \frac{x(A-x)}{A}$$

On differentiating this with respect to x it is apparent that the poise is a maximum when

$$x = \frac{A}{2}$$

that is when the oxidant and reductant are present in equal concentrations. It can also be shown that the poise increases with the total concentration of oxidised and reduced states.

The poor poise of well aerated soils is due to the absence of a reversible system in sufficiently high concentration. Oxygen is present at a high concentration but it does not function reversibly at the blank platinum electrode used for the determination of redox potentials of soils. Starkey and Wight (4) attribute the better poise of submerged soils to the high concentration of reduced products and to the presence of systems whose redox potentials are of the order of redox potentials of submerged soils.

The concentrations of oxidant and reductant are dependent upon certain factors such as complex ion formation and changes in pH.

Complex ion formation can have a marked effect on the oxidation-reduction potentials by inactivating a part of the oxidised or reduced phase. Since both iron and manganese have a tendency to form chelated complexes with certain components of soil organic matter, it may be inferred that pure iron and manganese systems undergo considerable modification in the soil.

The pH of an oxidation-reduction system affects the degree of ionisation and hence will alter the redox potentials. The E_h increases in many systems by about 0.060 volt for each unit fall in the pH value of the system. That is, the same system will have lower E_h values in the alkaline range than in the acid range.

This change in redox potential with pH can alter the relative position of a system on the redox scale and thus has great significance in the interpretation of redox potentials in soils.

The standard oxidation-reduction potential for the system $\text{MnO}_2 + 4\text{H}^+ + 2\text{e} = \text{Mn}^{++} + 2\text{H}_2\text{O}$ is 1.23 volts and for $\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e} = \text{NO}_2^- + 2\text{OH}^-$ is 0.0 volt. This means that the reduction of nitrate to nitrite can take place only after considerable amounts of MnO_2 are reduced. At pH 7.0 the standard oxidation-reduction potentials become 0.43 volt for the $\text{MnO}_2-\text{Mn}^{++}$ system and 0.41 volt for the $\text{NO}_3^-/\text{NO}_2^-$ system. Thus at pH 7.0 the reduction of MnO_2 and NO_3^- takes place almost simultaneously.

The $\text{Fe}^{+++}-\text{Fe}^{++}$ system is more dependent on pH. The standard oxidation reduction potential for the $\text{Fe}^{+++}-\text{Fe}^{++}$ system is 0.77 volt. Hence NO_3^- should not be reduced until considerable amounts of Fe^{+++} are reduced. But the findings of Pearsall (5) and Mortimer (6) show that Fe^{++} does not appear in appreciable amounts until NO_3^- has been completely reduced. The apparent disparity however disappears when it is realised that the standard potentials at pH 7.0 are 0.41 volt for the $\text{NO}_3^-/\text{NO}_2^-$ system and -0.10 volt for the $\text{Fe}^{+++}-\text{Fe}^{++}$ system. Thus at pH 7.0 iron is not reduced so long as nitrates are present.

Gillispie (7) measured the redox potentials in waterlogged soils and showed that reduction rather than acidity was responsible for their unfavourable crop-producing capacity.

(b) Oxidation and Reduction in Pedological Processes

There are some important pedological processes in which oxidation and reduction play an important role.

The process of podzolization that takes place in cool humid climates involves, among other associated reactions, the reducing action of easily oxidisable organic materials upon ferric oxide in rocks and soil materials. The iron is reduced to the ferrous condition, which is more soluble than ferric oxide at the pH value of podsol., that is 3.5 and 4.5. The soluble iron is translocated to the B horizon by the percolating waters. In this horizon reducing conditions are less pronounced because of the lack of easily oxidisable organic matter even though atmospheric oxygen now has less access to the iron than it had in the surface horizon. On being lodged in the B horizon, the recently precipitated ferric hydroxide is dehydrated by seasonal desiccation. Thereafter it is immune from further reduction. Manganese undergoes similar reduction in the organic horizon but is not so readily oxidised when removed from this horizon and hence may be translocated to lower depths. Like iron it is ultimately oxidised and subsequently dehydrated forming black deposits of manganese dioxide on the surface of cracks in the subsoil and in the underlying rocks. The reducing action of the forest litter has prevailed over the oxidizing action of the atmospheric oxygen.

In the process of laterization too, ferric iron and humus are involved but because of the notable differences in temperature the final products are different. Laterites are produced in humid tropical climates. The organic matter is itself rapidly and completely oxidised into its ultimate products, carbon dioxide and water. This oxidation is effected by microbial agencies, and their action is accelerated at high temperatures. Thus there is less reducing action derived from the organic remains. At the same time iron existing near the surface is also more markedly oxidized at high temperatures. This iron is also more completely dehydrated and is therefore immobile. Thus iron tends to remain in the A horizon of lateritic soil profiles.

The degree of acidity plays a part in both podzolization and laterization but oxidation and reduction also exercise an influence. In fact the more alkaline conditions under which laterization occurs is itself partly the result of oxidation. Rapid oxidation of the acid-forming organic residues together with the more rapid hydrolysis of minerals at high temperatures gives rise to the more alkaline conditions encountered in laterites.

(c) Ecology of Plant Life and Ecology of Microorganisms of the Soil.

The production of organic tissues in green plants is a process of reduction. The aerobic decomposition of organic tissues (organic matter) is a process of oxidation. The production of organic matter by photosynthesis is considerable. Since organic matter has no noticeable tendency to accumulate rapidly in soil, that is to say, its formation and decay are in equilibrium, it follows that reductive processes that help to form organic matter, and oxidative processes that tend to destroy organic matter are in equilibrium.

The aerobic decomposition of fresh organic matter can be divided into two phases:—

First phase .. Conversion into humus.

Second phase .. Breakdown of humus into simple gases and mineral constituents.

Humus is organic matter that has been so extensively decomposed that the organic structure is lost. It originates from the syntheses of microbial tissues and their metabolic products, and also from the accumulation of organic materials which are decomposed only with difficulty.

These two phases coincide with Winogradsky's (9) division of soil microflora into two groups —

(a) indigenous

(b) fermentative

(a) The numerous indigenous microflora remain fairly constant in numbers and have no large fluctuation. They require only the nutrients normally present in soil. Soil in this context excludes organic matter which has not been humified.

(b) Fermentative microflora are organisms which grow rapidly on fresh organic matter and are normally present in comparatively small numbers. With the addition of fresh organic matter these organisms multiply rapidly but after a time the numbers decline again to their former relatively low level.

Winogradsky regarded the indigenous flora as essentially small coccoid bacteria which Conn (10) considers to be stages in the life cycle of certain normally rod-shaped organisms of the genus *arthrobacter*. Conn went further and said that these forms are difficult to classify owing to their weak fermentative nature but are non-sporing and rod-shaped with either a *micrococcus* stage or in the shape of small rods of the genus *agrobacteria*.

Fermentative organisms would therefore include the rest of the sporing and non-sporing bacteria, actinomycetes and fungi. The fungi presumably exist as spores except where fresh organic matter is available.

Garrett (11) put forward the idea of colonisation, exploitation and exhaustion of the substratum of the soil resulting in a succession of microorganisms. He points out the close linkage which exists between the ecology of plant life and microbial ecology of the soil with one fundamental difference namely that the microbial succession depletes rather than builds up the capacity of the habitat. The result is that the end point of the action of a succession of microorganisms on a substratum is not a climax association but is exhaustion-zero. Among plants, on the other hand, the opposite is the case. Pearsall (12) showed that the distribution of natural types of woodland vegetation in Northern England was associated with soil properties which could be characterised by redox potentials and pH. From the above it can be seen to what extent oxidation and reduction affect the ecology of plant life and that of microorganisms in the soil.

(d) Oxidation-Reduction Systems in Soils.

There are a number of inorganic redox systems operating in soils. It is difficult to identify the organic systems as the soil organic matter is such a heterogeneous mass of organic substances in all stages of decomposition together with microbial cells and their metabolic products. There is evidence that bacteria influence the potential of the medium in which they function (2, 4, 13, 14).

Some redox systems in soils are shown below. In this list the highest level of oxidation is represented by the oxygen potential and the highest level

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of reduction is indicated by the hydrogen potential. It is possible for any system to oxidize those below it.

<i>Electrochemical Reaction</i>	E_0 volts	E_0 at pH 7.0 volts
$O_2 + 4H^+ + 4e = 2H_2O$..	1.23	0.82
$Fe^{+3} + e = Fe^{+2}$..	0.77	—
$MnO_2 + 4H^+ + 2e = Mn^{+2} + 2H_2O$..	1.23	0.13
$NO_3^- + H_2O + 2e = NO_2^- + 2OH^-$..	0.00	0.41
Fumarate + $2H^+ + 2e =$ Succinate ..	—	-0.03
Oxalacetate + $2H^+ + 2e =$ Malate ..	—	-0.10
$Fe(OH)_3 + e = Fe^{+2} + 3OH^-$..	0.77	-0.10
Pyruvate + $2H^+ + 2e =$ Lactate ..	—	-0.18
Acetaldehyde + $2H^+ + 2e =$ Alcohol ..	—	-0.19
$SO_4^{-2} + 3H_2O + 6e = S^{-2} + 6OH^-$..	-0.61	-0.20
$2H^+ + 2e = H_2$..	0.00	-0.41
$SO_4^{-2} + H_2O + 2e = SO_3^{-2} + 2OH^-$..	-0.90	-0.40

As there is an unlimited supply of oxygen in a well-drained soil the oxygen system would dominate the redox potential. But the redox potentials of well-drained soils as measured with blank platinum electrodes do not tally with the values predicted by theory. Cooper (15) explains this disparity by suggesting that the blank platinum electrode, used for determination of redox potentials, functions as an irreversible oxygen electrode owing to the formation of an oxide film. Pearsall and Mortimer (6), however have extrapolated some of Cooper's figures and have obtained values of the order encountered in aerated soils.

The iron system comes next in importance. In fact, Bradfield, Batjer and Oskamp (16) have even suggested that it is the predominant system in soils. They adduce the following reasons for the importance of this system: (i) the abundance of iron in soils, (ii) the increase in concentration of ferrous iron when soils are waterlogged, (iii) the similarity of behaviour of sulphuric acid extracts of soils to that of the ferric-ferrous system when titrated potentiometrically, (iv) the redox potentials of soils lie within those of the iron system.

The MnO_2 — Mn^{+2} system is also widely distributed in soils. Like Fe^{+2} , Mn^{+2} is readily oxidized by atmospheric oxygen so that the concentration of Mn^{+2} is also determined by the oxygen tension and pH.

The NO_3^- — NO_2^- system is practically at the same level on the redox scale as the MnO_2 — Mn^{+2} system. Pearsall (5) observed that soils containing nitrate had redox potentials exceeding 350 millivolts at pH 5. Mortimer (6, 17) records that nitrate was rapidly reduced when the redox potential fell below 0.4 volt at pH 7.0. Aoki (18) noted a rise in redox potential on the addition of nitrate to a reduced soil.

The findings of sewage investigators are of interest in this connection. Fales (19) reported that the addition of sodium nitrate to the river prevented the anaerobic decomposition of paper mill and tannery effluents with the accompanying offensive odours. Sanborn (20) found that the addition of sufficient sodium nitrate gave complete protection against odours in the treatment of cannery wastes in lagoons. Heukelekian (21) observed that sodium nitrate retarded sulphide formation in sewage and attributed this effect to the preferential reduction of nitrate rather than sulphate. Finally Moore and Ruchhoft (22) observed that in a sewage solution containing 135 p.p.m. sodium nitrate the E_h dropped gradually from +0.3 volt to +0.1 volt and remained at this level, whilst without nitrate the potential dropped to -0.1 volt within six hours.

From the above it is clear that the presence of nitrate (1) retards reduction, and (11) stabilizes the potential at 200-400 millivolts at pH 7.0.

It can be seen from the table given earlier that at pH 7 with the disappearance of nitrate typical reducing conditions will follow. Pearsall (5) states "that the soils examined undergo an alteration in properties in the vicinity of E_s 320-350 millivolts, such that below that point products of reduction are demonstrable whilst above it oxidation products are more prominent. If these characteristics are of general application it seems that soils below E_s 320 should be regarded as effectively reducing whilst those above E_s 350 are predominantly oxidizing". After further researches Pearsall and Mortimer (1) state "In all cases so far examined in soils, waters, and muds representing a variety of natural conditions, products of oxidation (Fe^{+3} , NO_3' , SO_4') are found above the potential zone E_s +350 millivolts below this zone their reduced counterparts are present".

The fumarate-succinate, oxalacetate-malate, pyruvate-lactate and acetaldehyde-alcohol systems are all organic biological systems which make appreciable contributions to the redox potentials in submerged soils.

(e) Factors Influencing the Oxidation-Reduction Potentials of Soils.

The factors which influence the oxidation-reduction potentials of soils are the degree of aeration, the content of readily decomposable organic matter and the base status of the soil. Good aeration, absence of excessive microbiological activity, and a low base status are conducive to high potentials. The opposite conditions are favourable for low redox potentials.

Peech and Boynton (23) in their studies on orchard soils noted that water-logging caused a marked drop in potential only in soils containing readily oxidizable organic matter and they attempted to correlate susceptibility to reduction on water-logging to their C:N ratio. According to Pearsall (24)

this ratio must exceed 20 for a marked drop of potential to occur on water-logging. The association between organic matter and redox potentials suggests that microbial activity is involved.

(f) Influence of Low Oxidation-Reduction Potential on Submerged Rice Soils and on the Rice Plant.

That rice roots exude oxygen has been demonstrated by Van Raalte (25) by ligaturing of rice roots, by Mitsui (26) by using a redox indicator and by Kumada (27) by using luminous bacteria. As the rice roots exude oxygen and maintain an oxidized environment, the redox potential per se could have little effect on the rice plant. But the reducing intensity can have a marked effect on the concentration of substances which in turn can produce an injurious effect on rice roots if they are present in excess. Under low redox potentials the rice plant would be deluged with reduced products especially Fe^{+2} , Mn^{+2} and H_2S , and though young roots and tips of older roots exude oxygen and maintain an oxidized environment, there is a limit to this protective device which is likely to be reached when an acid soil with a high content of iron, manganese and sulphate attains low redox potentials.

The first report on redox potentials of Japanese paddy soils was made by Osugi (28) in 1934. In 1937 Shioiri and Aomine (29) observed that nitrification occurs at the surface of submerged paddy soils and showed that there is a difference between the surface layer and the underlying layer. Later Shioiri and Aomine (30, 31, 32) found two or more surface sub-layers of different colours the uppermost layer was a few millimetres in thickness and yellowish in colour while the underlying layer was greyish or bluish indicating the presence of reducing conditions. Between these two layers was a thin brownish layer. The redox potential of the upper layer was invariably above 300 mv at pH 6 and the redox potential of the lower layer was definitely below this. Oxidised products such as nitrate, sulphate, ferric iron are found in the upper layer and reduced products such as ammonia, sulphide and ferrous iron are found in the lower layer. Shioiri and Aomine termed the upper layer as "oxidised layer" and the lower layer as "reduced layer". After the discovery of the middle layer, Aomine (33) called it the "iron deposit layer". He also noted the existence of more than two iron deposit layers, analogous to Liesegang rings.

Rodrigo and Pollard (34) determined the redox potentials of the supernatant liquids and found they were in the oxidising range. Rodrigo (35, 36) demonstrated the stratification of redox potential of submerged paddy soils. He submerged different paddy soils and determined the variation of redox potential at depths of 6", 4" and 2" from the surface of the soils. At a depth of 6" the redox potential decreased and reached more or less constant values after 80 days of submergence. At a depth of 4" redox potential of the soil at first decreased and thereafter began to rise. At a depth of 2" redox potential first

decreased, but not to that of 4" depth, and then increased. Rodrigo observed that on submergence ammonia, iron, manganese and oxidisable matter increased with time, then reached a peak and finally decreased. He postulated that ammonia formed in the bulk of the soil diffuses upwards on a concentration gradient and when it reaches the oxidised layer is converted to nitrate. The nitrate thus formed again in a concentration gradient diffuses downwards and when it reaches the reducing layers of the soil denitrification takes place. During denitrification nitrate acts as an oxygen donor to oxidise the reduced iron, reduced manganese, oxidisable matter, etc., and nitrogen escapes as a gas. The variation of redox potential of the soils at different depths indicates that denitrification takes place and under the conditions of his experiments it was found that denitrification takes place above a depth of 6" from the surface of the soil.

Ozugi (28) noticed that an increase in the amount of ferrous iron in submerged soils is accompanied by a drop in the redox potential. Ponnampereuma's (3) findings lead to the same conclusion. Yamada and Ota (38) confirm this. Patrick *et al* (39) found that at pH 5.1 nitrate nitrogen was reduced at Eh of 300 millivolts. At -100 mv, nitrate nitrogen was lost at the rate of 15.9 ppm per day. It was evident that nitrate nitrogen was very unstable at this potential. The reduction of nitrate nitrogen was also shown to be biological as sterilized soils did not reduce nitrate nitrogen. Miers *et al* (40) determined the effect of oxidation-reduction potential of the soil on the germination of rice. They noticed that with the lowering of the redox potential the percentage of germination is lowered. Their results are given below—

<i>Redox-Potentials</i> <i>Millivolts</i>				<i>%</i> <i>Germination</i>
-88	7.8
100	20.1
300	22.6
400	38.9
450	53.5
500	93.7

The practical significance of this is seen when paddy is sown broadcast, small shallow drains being made within the *liyadda* (field) to drain off water in order to ensure that there is no trace of stagnant water in the field. The germination of paddy in these small drains is poor while outside the drains it is quite good.

The microbe metabolism in submerged paddy soils could be divided into three steps: oxybiontic metabolism of aerobes and facultative anaerobes, anoxybiontic metabolism of facultative and strictly anaerobic heterotrophs, and thirdly methane fermentation and sulphate reduction by strict anaerobes. These three stages have specific ranges of redox potentials. The redox potential required for sulphate reduction is estimated at about—200 mv by McCabe and Eckenfelder (37), while that of methane fermentation has not been definitely established, but is likely to be either at the same level or at an even lower potential.

Organic matter in soils decomposes under aerobic conditions as well as under anaerobic conditions. The final products of decomposition however differ as indicated in the following schedule :—

<i>Reducing</i>		<i>Source</i>	<i>Oxidizing</i>
CH ₄ , CO C	.. CO ₂
N ₂ , NH ₃ , NO ₂ N	.. NO ₂ , NO ₃
H ₂ S S	.. SO ₄
PH ₄ P	.. PO ₄
Fe ²⁺ Fe	.. Fe ³⁺
Mn ²⁺ Mn	.. Mn ³⁺
Cu ⁺ Cu	.. Cu ²⁺

In general, the oxidized forms constitute the nutrient sources for plants, The reduced products, though generally present only in low concentrations, are nevertheless toxic to most of the cultivated plants.

Flooding of soils is followed by the depletion of oxygen and lowering of redox potential, in consequence of which marked microbiological changes take place. The microfloral changes are both qualitative and quantitative. The beneficial effects of flooding are the eradication of fungi such as *Sclerotinia Sclerotiorum* (Stoner and Moore 41) and nematodes like *Heterodora Marioni* (Brown 42). Flooding is also used as a means of elimination from the soil of *fusarium oxysporum* F. *Cubense* (Stover 43). That the pathogenic fungus *Fusarium moniliforme* (G fujikurri) is controlled to a fair extent by flooding was observed by Bertus and Abeygoonewardane (44).

Ramiah (45) reports physiological diseases of rice from various countries under various local names. These diseases have caused serious losses in yield and in some cases were severe enough to cause the death of the plant. The main symptoms are discoloration of leaves, stunted growth and damaged root system. The Ministry of Agriculture and Forestry, Tokyo (46) is of opinion that the physiological disease observed in the degraded rice soils of Japan is due to the production of hydrogen sulphide. Sik (47) working in Hungary observes that the addition of small amounts of hydrogen sulphide or ferrous iron to a culture solution produced symptoms of rice browning. Vamos (48) ascertained

by field survey and microbiological study that hydrogen sulphide is the cause of browning of rice plant in Hungary. Ponnampereuma, Bradfield and Peach (49), Ponnampereuma (50, 51) are of opinion that high concentrations of ferrous iron in the soil solution are responsible for the disease. Leveque and Mile Beley (52) working in France with hydroponic culture observed toxicity due to ferrous iron at 200 ppm in the culture solution. Ota and Yamada (38) found in pots "where iron was applied to paddy land reductive soil, almost all plants were dead due to severe occurrence of *akagare* (ferrous iron toxicity). lowering of yield due to iron application was more remarkable with the soil of lower Eh value". It is possible that the reports of disease from different countries may not refer to the same disease and the cause of the disease may also be different. The literature cited above shows that the disease is attributable to the reducing conditions associated with low-redox potentials which prevail in submerged rice soils no matter what actual agent is involved.

Root respiration inhibitors such as hydrogen sulphide and butyric acid produced in submerged paddy soils under conditions of low redox potentials affect the uptake of ions such as phosphorus, potash and silica, and predisposes the rice plant to disease such as *Helminthosporium* (Mitsu, 53). Osugi and Kawaguchi (54, 55) found that the root rot disease of the rice plant was caused by sulphide produced in certain submerged soils by the reduction of ammonium sulphate at low redox potentials.

Vamos (48) put forward the idea that low redox potentials associated with toxic reduced products, specially hydrogen sulphide, is the chief cause of the disease in paddy. *Piricularia Oryzae* and other fungi are secondary manifestations of the disease, the primary cause of which is the presence of toxic products resulting from anaerobic microbial activity. Depending on the reaction (pH) some of the sulphide ions form molecular H_2S , while some form SH^- ions; H_2S affects the roots, while SH^- ions are taken up by the roots and damage the tissues of the nodes. Both cause metabolic disturbance in the plant. In the first case the roots die and *Piricularia* sets in; in the latter case *Piricularia* seldom appears and the sterile panicles stand rigidly upright ("straighthead"). Baba *et al* (56) stated that fungi make their appearance on the plants only after metabolic disturbances have supervened. They postulated that the manifestation of the disease may vary due to differing resistance of the plants to the disease or to dissimilar nutrient conditions and to different meteorological conditions. These different manifestations are probably the basis of the widely different names ("bianchetta", "gentilomo", "crodatore", "carolo", "dry leaf disease", "pansuk", "sental", "akagare", "akiochi", etc.) which are used for the disease in different countries. Applications of $CaCO_3$, CaO , "red slime", upland red earth have shown beneficial results but have not achieved complete control over the disease. Successful results were obtained with nitrate. Nitrates inhibit sulphate reduction and therefore the formation of H_2S .

Finally Eri (57) attempted the classification of paddy soils with respect to redox potential.

(g) The Measurement of Oxidation-Reduction Potential.

The oxidation-reduction potential may be measured by a potentiometric hookup in a manner similar to that used in pH measurements, except that a bright platinum electrode is used in place of a bubbling hydrogen, quinhydrone, or glass electrode. A calomel half cell is used as the reference cell and the voltages are finally referred to the normal hydrogen electrode taken as zero. Calomel cells have the following values compared with the normal hydrogen electrode at 20° C :

Saturated calomel cell	=	+0.249 volt
Normal calomel cell	=	+0.285 volt
Tenth-normal calomel cell	=	+0.337 volt

The above values have to be added to the observed readings to express the results in relation to the normal hydrogen electrode taken as zero.

The E_h -pH relationship may be compensated by two methods. Bradfield *et al* (16) suspended soil samples in 0.2N sulphuric acid instead of water. The acid buffers many soil systems near pH 3 so that the readings need not be corrected. Moreover the acid brings larger quantities of the iron present in the soil into the ionic state and thereby increases the stability (poise) of the system. On the other hand it might have a greater solvent action upon the oxidants than upon the reductants in soils and hence distort the results. The other method is to determine the E_h -pH relationship for the soil by titrating potentiometrically to various pH values and determining the E_h at each pH value. When plotted, the E_h change for unit change in pH may be determined and all values may then be expressed at the same pH. This method is also open to criticism unless the E_h -pH relationship is determined in every sample, as no two horizons of the same soil profile will have the same E_h -pH relationship. Jeffery (58) considered the ferric-ferrous system to be the dominant redox system in submerged soils and offered a theoretical proof of why the factor—180 mv should be used for the E_h -pH slope. Researches carried out in the Division of Soil Chemistry of the International Rice Research Institute, Philippines (59) indicate that the iron system may not be the dominant redox system in submerged rice soils and it is possible that organic constituents may qualify for the role of the dominant redox system, and organic reduction products may contribute more than ferrous iron towards the smothering of rice roots in highly reduced soils. Their work shows that for a given soil the E_h -pH slope may vary with the time of submergence at a given time of submergence the E_h -pH slope may vary from soil to soil

organic matter may alter the Eh—pH slope for any soil at any stage of reduction and the Eh—pH slope of a reduced soil is not linear throughout the pH range and varies markedly with pH.

Many workers take the course of using a single value such as 0.060 volt for all soils. This appears to be the best for comparative purposes.

The best method of making the platinum electrode is given by Quispel (60). Platinum wires 0.5 mm. thick and 2 cm. long, which have been melted into glass tubes 0.5 cm. in diameter, are used as electrodes. The length of the wire protruding from the glass is ± 1.5 cm. Contact with copper wire leading to the potentiometer is made by soldering as recommended by Buehrer *et al* (61). The platinum electrodes should be cleaned in hot chromic acid, rinsed in distilled water, and heated over an alcohol flame.

All platinum electrodes should be critically examined before they are used for redox measurements in soils. Small differences between electrode readings in a buffer (a saturated solution of quinhydrone in 0.05N potassium hydrogen phthalate has a redox reading of 0.223 volt and a saturated solution of quinhydrone in 0.1N hydrochloric acid has a redox reading of 0.392 volt against a saturated calomel electrode at 20° C) (62) may be greatly amplified in redox potential measurements in soils. The electrodes are hung close together in a beaker containing a buffer solution and the Eh is measured at each electrode. Electrodes showing potentials differing more than 10 millivolts from the mean value should be rejected. Usually chromic acid treatment tends to cause too high a value when the electrodes are used immediately after treatment. The electrodes are allowed to age, preferably in the soil, before readings are taken. It is best to measure the redox potentials *in situ* and to place the platinum electrodes permanently in the soil.

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