Dynamic Behavior of Ferrous Iron in Paddy Soils

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Iron in soils occurs in the forms of primary and secondary minerals, hydrated oxides and their organic and inorganic derivatives. Iron forms in soils, however, are not so stable so that they may be easily converted to more stable ones in accordance with environmental soil condition. Transformation of iron compounds dramatically takes place, particularly in paddy soils because of the alternation of submergence and drainage.

Under submerged condition, the brown or reddish brown in soil color changes to bluish-green or black shades, and large amounts of iron are brought into solution due to a remarkable formation of ferrous iron. On the other hand, drainage of irrigation water after the rice growing season accelerates the occurrence of oxidative sediments such as iron and manganese.

Until rather recently, the behavior of iron in paddy soils has been mainly focussed on soil chemistry in relation to degraded paddy field[2,6,8] or iron toxicity[10]. The fruits of the studies have been established as the chemistry of paddy soil[5,7] and have contributed to high production of lowland rice. However, the effects of ferrous iron on the physico-chemical properties of paddy soils have not been evaluated sufficiently because of their complicated nature and behavior.

This paper is the outline of "Dynamic Behavior of Ferrous Iron in Paddy Soils" published in the Bulletin of the National Institute of Agricultural Sciences, Series B. 21[4].

Reduction of iron compounds in paddy soils

The transformation of ferric iron in paddy soils has been repeatedly investigated in order to determine what effects these have on the growth of rice plant or their influence on profile development.

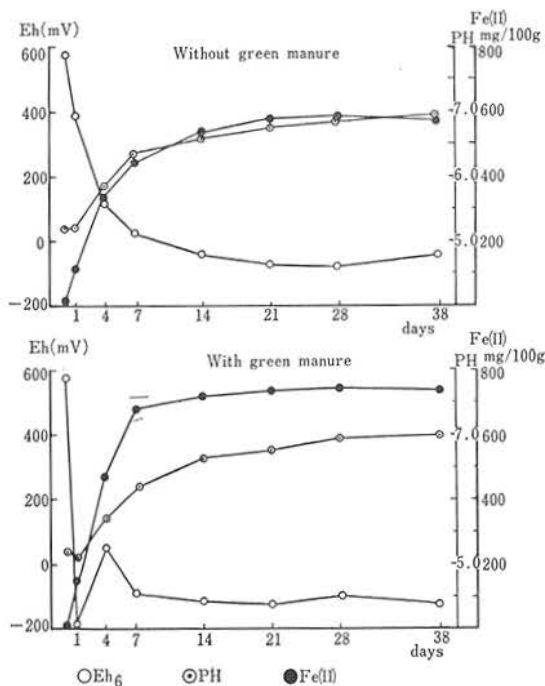There are various factors strongly affecting the reduction of iron compounds. The forma-

Fig. 1. Periodical changes in redox potential, soil pH & Fe (II).

tion of ferrous iron depended upon the easily decomposable organic matter contents and the amounts of free iron oxide, being closely related to the lowering of redox potential, and to the rise of soil pH. An example of greyish brown soil with or without green manure is shown in Fig. 1. An application of organic matter to soil brought about progressive formation of ferrous iron and proceeded in parallel to ammonium formation. Such reaction was related to anaerobic decomposition of organic matter. As shown in Fig. 2, high correlation
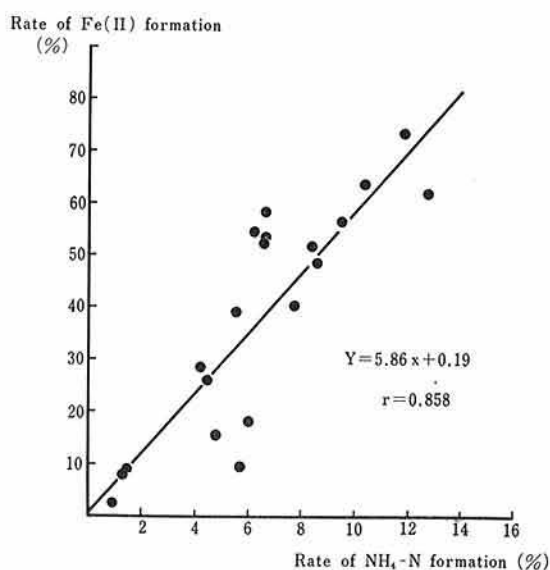
Rate of Fe(II) formation (%)

Fig. 2. Relationship between ammonium formation & Fe (II) formation.

was found between the rate of ferrous iron formation (the rate of ferrous iron to free oxide determined by Aguilera and Jackson) and that of ammonium formation (the rate of ammonium to total soil nitrogen).

In the case of slightly acid or neutral reaction, the total amount of produced ferrous iron was at a maximum. At temperatures lower than 10°C reduction process advanced very slowly, and with the raising of temperature, more remarkably.

The presence of nitrate nitrogen retarded the reduction of iron, the effect increasing with nitrate concentration. In the presence of sugars, nitrate nitrogen did not prevent the reduction. On the other hand, ammonium nitrogen enhanced the mobilization of iron in soils as the result of the promotion of biological action by NH_4.

These facts illustrate that all soil conditions controlling the reduction of ferric iron were associated with the efficiency of microbiological function. In other words, the formation of ferrous iron in paddy soil under submerged condition depended to a large extent upon the action of soil microbes.

Takai, et al[1, 9] have thrown light on the microbiological mechanism of the reductive process, and clarified the pathway to biochemical reduction of iron in this process.

Ferrous iron forms in submerged soils

When soil is submerged, large amount of ferric iron is rapidly converted into ferrous state through chemical and/or biochemical process. Although ferrous iron is more soluble than ferric state, the concentration of ferrous iron in the solution is relatively small owing to the precipitation of ferrous hydroxide, carbonate, sulfide, and so on. The precipitation reactions are governed by ionic equilibria involving Fe^{2+}, OH^-, carbon dioxide and hydrogen sulfide.

Ionic ferrous iron which is partly dissociated from both insoluble and soluble ferrous iron compounds, is adsorbed on soil colloids exchangeably or strongly, or fixed, according to the kinds of the clay minerals or exchangeable sites.

Furthermore, ferrous iron exists as one of the components in primary and secondary minerals, and also as inorganic complexes combined with silicates, and some organic compounds in soil combine with ferrous iron compounds. The interrelation between the various iron forms and their equilibria in submerged soil is schematically given in Fig. 3.

Thus, ferrous iron compounds exist as highly complicated forms. In addition, these ferrous iron forms are under physico-chemical equilibria corresponding to soil circumstance
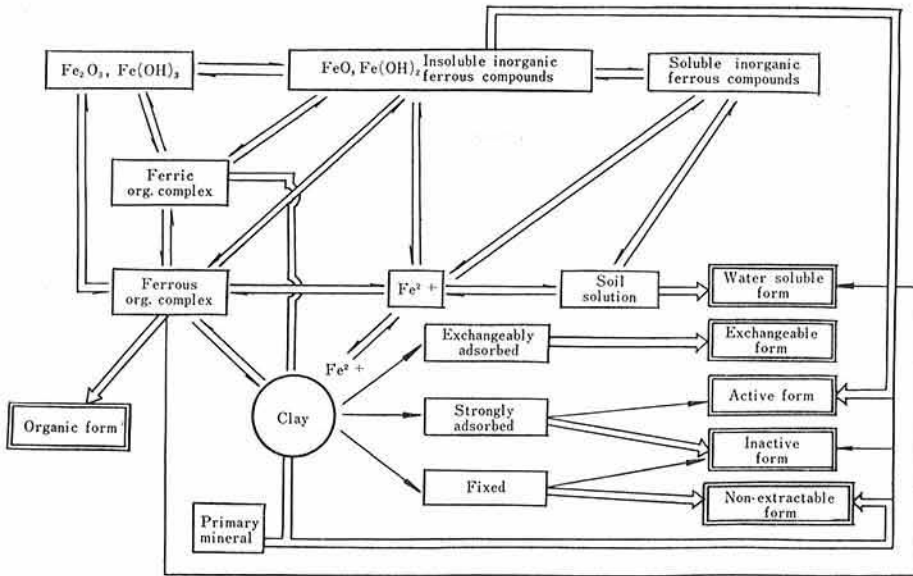
Fig. 3. Schematic representation of equilibrium of various ferrous iron forms.

or condition. It is impossible, at present, to fractionate all individual forms of ferrous iron compounds in reduced soils. For convenience, ferrous iron forms are divided into five forms from the viewpoint of their chemically binding status, as follows:

1) Water soluble form: This is mainly ionic and soluble ferrous iron in soil solution, and includes soluble ferrous organic complexes.

2) Exchangeable form: This is exchangeably adsorbed on clay mineral and exchangeable site.

3) Active form: This is mainly precipitated as insoluble forms and in part strongly adsorbed on clay mineral.

4) Inactive form: This is mainly strongly adsorbed on clay mineral and partly derived from primary and secondary minerals and includes a part of insoluble forms.

5) Non-extractable form: This is combined with clay mineral and exists as a constituent of primary and secondary minerals.

Water soluble and exchangeable forms were readily oxidized to ferric state, but inactive and non-extractable forms were oxidized very slowly, showing their rather high stability against atmospheric oxidation.

Under hydrogen gas (nitrogen gas) flow,

the above-mentioned ferrous iron forms can be continuously extracted without undergoing any ionic changes from the same soil sample by successive leaching of various extractants, that is, boiled distilled water cooled at room temperature for water soluble, neutral N-KCl for exchangeable, 0.2% $AlCl_3$ and pH 3.0 N-NaOAc for active, and 0.2 N-HCl for inactive forms. Non-extractable ferrous iron form is calculated as the subtraction of the total extractable ferrous iron from the total ferrous iron determined by $HF-H_2SO_4$ digestion method.

Characteristics of ferrous iron forms in paddy soils

As described before, ferrous iron in submerged soil exists in many complicated forms. Fig. 4 shows the rate of increase of various ferrous iron forms induced by submergence of various paddy soils.

Generally speaking, paddy soils analyzed were divided into three groups from the viewpoint of the characteristics of ferrous iron status as follows:

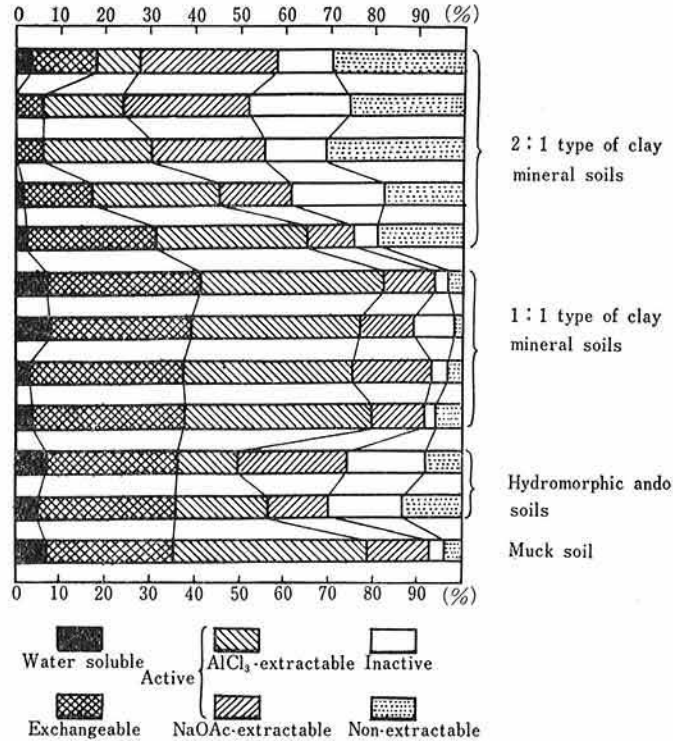**1) Those having large amounts of inactive**

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Fig. 4. Increase rate of ferrous iron forms induced by submergence.

and non-extractable forms, but a little of water soluble and exchangeable forms. This group belonged mainly to 2:1 type (of clay mineral) soils.

2) Those having large quantities of exchangeable and $AlCl_3$ extractable forms, though not without small amounts of inactive and non-extractable forms. This group belonged mainly to 1:1 type (of clay mineral) soils.

3) Those having relatively average amounts of each of the ferrous iron forms. This group belonged to hydromorphic ando soils and muck soils.

Each soil group possessed large amounts of active form, but 2:1 type soils contained more N-NaOAc extractable form compared to 1:1 type soils.

During the reduction process, formation of water soluble and exchangeable forms reached maximum within a relatively short time, but the equilibria in the active and inactive forms

were somewhat delayed.

An application of organic matter to soil brought about an increase of each of the ferrous iron forms, especially of water soluble form, due to the activation of soil microbes and probably also to the chelation between iron and organic compounds metabolized by microbial action.

Effects of ferrous iron on some physical properties

It seems reasonable that the aforementioned characteristics of ferrous iron forms in paddy soils are affecting the physical properties of paddy soils.

Sedimentation volume increased in proportion to the increasing amounts of produced ferrous iron because of changes in colloidal structure. Such structural changes in soil colloid may be intimately connected to large quantities of ferrous iron and water adsorbed on

soil colloids. This highly hydrated colloidal structure is closely associated with the jelly-like structure of gley horizon in which bulk density is very low.

As seen in Table 1, water permeability coefficients became lower with the advance of reduced condition. The reason for this is also attributable to the changes in colloidal structure. The adsorbed water on soil colloid is immobile and not effective for permeability. This fact may explain the lower water permeability of gley horizon despite a large amount of porosity.

Table 1. Effect of reduction on water permeability coefficient

Samples	Bulk density gr/ml	Porosity %	K20* cm/sec
Grey soil			
Natural structure	1.10	54.4	4.9×10^{-4}
Air dry sieved	0.93	64.9	8.3×10^{-6}
Reduced soil	0.99	62.7	2.0×10^{-6}
Reduced soil with glucose	0.85	67.8	4.0×10^{-6}
Strong gley soil			
Natural structure	0.75	71.7	1.8×10^{-6}
Air dry sieved	0.86	67.5	1.7×10^{-5}
Reduced soil	0.96	63.8	1.8×10^{-6}
Reduced soil with glucose	0.94	64.5	1.8×10^{-6}

* Water permeability coefficient

Both cutting strength and crushing strength are an index of soil cohesion closely associated with capillary power. The increase of oxidative sediments such as iron and manganese oxides brought about an increase in both strength properties, because such oxides work as a good cement for binding soil particles together. The ready formation of oxidative iron mottling is closely related to the characteristics of ferrous iron forms in reduced soils as pointed out before.

Some aspects of paddy soil profile development

Paddy soils exhibit some prominent features such as formation of gley horizon (reduced layer), iron mottling, manganese concretion, etc. Therefore, such morphological features are fundamental criteria for the classification of paddy soils.

High quantities of ferrous iron exist as soluble form in gley horizon. Consequently, in soil survey, α,α'-dipyridyl solution is effectively used for the detection of gley horizon. However, some exceptions had been observed particularly on gley horizon from marine alluvial soils in spite of the apparent bluish or greenish grey in soil color. One possible explanation to this is the fact that α,α'-dipyridyl reaction is intimately connected to the characteristics of ferrous iron forms: Soils having high amounts of water soluble, exchangeable and active forms instantly react with this reagent to show dark reddish color, but soils having high contents of inactive and non-extractable forms gradually show only faintly pink color.

In the same way, iron mottlings easily form in soils which dominantly contain water soluble and exchangeable forms susceptible to oxidation, but iron oxidative sediments cannot be found in soils which contain high contents of inactive and non-extractable forms. In such soils, however, iron mottlings occur more distinctly with the age of cultivation owing to the increment of water soluble and exchangeable forms by the progressive enrichment of organic matter as a result of rice cultivation.

It can also be indicated the importance of colloidal iron in affecting the formation and stability of soil structure.

Although soil particles in the plowed layer are dispersed with the development of reduction because of the dissolution of cementing materials, soil particles are flocculated to show jelly-like structure similar to gley horizon with the increasing formation of ferrous iron. After the drainage at the harvest season of rice plant, soils are gradually drying up from the surface. During this process, soil particles are aggregated solidly as the result of irreversible dehydration of cementing materials and action of colloidal clay and organic matters.

Ferrous iron susceptible to oxidation, ferrous iron adsorbed on soil and hydrated ferrous iron precipitated in soil pores are im-

mobile by irreversible dehydration and oxidation, and combine soil particle together. An increase of water soluble and exchangeable forms promotes iron movement through the profile and enhances oxidative iron sediments effectively for an increase of mechanical strength that is an index of stability of soil structure. Kawaguchi and Kida[3] have indicated a very close relationship between the amount of free iron and the quantity of water-stable aggregate in paddy soils.

In this manner, the characteristics of ferrous iron forms in paddy soils are distinguishably reflected on the profile development.

In conclusion, this paper has pointed out that ferrous iron plays an important role not only in the formation of paddy soil profile, but also in the development of physico-chemical properties. However, it is suggested that the study of ferrous iron in relation to physico-chemical behavior of soils should be more emphasized in the near future.

Acknowledgement

References

1) Kamura, T., Takai, Y. et al: Microbial Reduction Mechanism of Ferric Iron in Paddy Soil. Soil Sci. and Plant Nutr., 9, 171, 1963.

2) Kawaguchi, K. and Osugi, S.: On the Reduction of Am-Sulfate in Paddy-Rice Field. J. Sci. Soil and Manure, 16, 123, 1942.

3) Kawaguchi, K. and Kida T.: Mechanical and Chemical Constituent of Water Stable Aggregates of Paddy Soil with Relationship to the Aggregate Size. Soil and Plant Food, 3, 22, 1957.

4) Motomura, S.: Dynamic Behavior of Ferrous Iron in Paddy Soils. Bull. Nat. Inst. Agri. Sci. B. 21, 1, 1969.

5) Ponamperuma, F. N.: The Chemistry of Submerged Soil in Relation to the Growth and Yield of Rice. Thesis, Ph. D. Cornell Univ. 1955.

6) Shiga, K.: Studies on Behavior of Hydrogen Sulfide in Paddy Soil. Thesis, Ph. D. Hokkaido Univ. 1962.

7) Shioiri, M.: Chemistry of Rice Field Soils. Dainihon Nokai 1943.

8) Shioiri, M. and Yokoi, H.: The Leaching Mechanism of Iron Sulfide. J. Sci, Soil and Manure, 20, 157, 1949.

9) Takai, Y., et al: Microbial Metabolism in Reduction Process of Paddy Soil. (Part 1) Soil and Plant Food, 2, 63 1956, (Part 2) Soil Sci. and Plant Nutr., 9, 176, 1963.

10) Takijima, Y.: 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. Bull. Nat. Inst. Agri. Sci., B. 13, 117, 1963.