

# Distribution and Improvement Of Acid Sulfate Soils in Japan

By HIDEYUKI MURAKAMI

Chief, Soils and Fertilizers Section, Shimane Agricultural Experiment Station

Studies on the acid sulfate soils in Japan started with the work of Kobayashi<sup>1)</sup> who observed a phenomenon that leaves of rice plants changed blackish brown in color from the tip dying before long, and showed that it was a damage due to  $\text{FeSO}_4$  produced from  $\text{FeS}_2$  by oxidation in the soil. After that Yoneda<sup>2)</sup> made studies of the distribution and origin of acid sulfate soils, and of the composition of the sulfides. Tanaka<sup>3)</sup> studies causes of the damage by sulfate soils to plants and the countermeasures.

## Distribution

Acid sulfate soils are distributed mainly in reclaimed lands along the coast of bays and lakes. Among the acid sulfate soils in Japan there are an area covering about 5,000 ha which has been improved and does not cause damage to crops now, an area more or less dangerous to crops at present covering about 4,000 ha and the rest feared to be dangerous to crops when it is reclaimed or the soil is brought to another place for addition. The last is estimated to be about 17,000 ha in area.

In the studies of the bottom mud of Lake Nakaumi, the author<sup>4)</sup> observed that acid sulfate soils are distributed in such places as fresh water came into contact with salt water and the movement of water was restricted by the configurations of the ground in lakes, bays or inlets. The bottom mud around the mouth of a river or in the shore of a city area is especially high in the content of oxidizable sulfur.

In such places fresh water or salt water lower in concentration makes the surface layer, while salt water higher in concentration stays stagnantly in the bottom. The salt water stagnant in the bottom is supplied with planktons and other organic matters from the upper fresh water, and there develops reduced condition resulting in accumulation of sulfides as the result of reduction of sulfates contained there. Acid sulfate soils are also distributed in such lakes as have had an effect of salt water in their history though they are now of fresh water.

## Forms of oxidizable sulfurs and methods of their analysis

Most of the oxidizable sulfurs are hydrochloric acid insoluble sulfides.<sup>5), 6)</sup> And examinations of samples collected from various places showed that they were mainly pyrites.<sup>5), 6), 7)</sup> A small amount of  $\text{H}_2\text{S}$ , free sulfur and organic sulfur is also found besides pyrites. In case pyrites are very high in content the quantity of S often amounts to 20 mg per 1 g of soil.

It requires much trouble to oxidize pyrites with nitric acid or to reduce them with tin for quantitative analysis. The author, therefore, proposed a simple method of analysis,<sup>8)</sup> that is, oxidation of pyrites with  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{SO}_4$  and titration of the latter with 0.1 N NaOH solution. When a sample equivalent to 1~2 g of dried soil is treated with 10 ml of 30%  $\text{H}_2\text{O}_2$  solution, about 80% of the oxidizable sulfur becomes  $\text{SO}_4$ . The content of oxidiza-

ble sulfur, the pH of the soil after oxidation and the amount of lime required are estimated by this method. This is a very effective method for surveys in the field. The quantitative analysis of  $\text{SO}_4$  after the titration is also performed.<sup>2)</sup>

### Growth-inhibiting components produced by acidification

Changes in the content of Al, Fe and Mn in the upland farm soil of the reclaimed land at Shimata where cultivation started in May, 1960 are shown in Table 1.<sup>9)</sup> At the beginning of acidification, there were sufficient amount of soluble Al, Mn and Fe to inhibit the growth of crops there. However, most of the  $\text{Al}^{3+}$  and  $\text{Mn}^{2+}$  were washed away by rain, and the greater part of  $\text{Fe}^{2+}$  was precipitated by oxidation becoming insoluble. The water soluble components thus nearly disappeared four years after, but  $\text{Al}^{3+}$  soluble in KCl solution increased in amount and the colloid became a heavily unsaturated form. Farm crops can not grow also in such a condition unless the acidity is neutralized. There is still a large quantity of  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the

subsoil.

### Damage to rice crop and the countermeasures

Lysimeter experiments were carried out combining such treatments as flooding of a paddy field throughout a year not to oxidize oxidizable sulfurs—a treatment to avoid strong acidification of the soil, positive promotion of the oxidation of sulfur during the second cropping period liming and water percolation.<sup>10)</sup> The treatments and yields in this experiment are shown in Table 2. In the 1st-5th lots the field was drained during the period of the second cropping to promote the oxidation of sulfur, and then flooded to grow rice plants (the soil treated in this way will be cited as acidified one).

In the 6th lot the field was flooded throughout a year (unacidified soil). During the period of rice cultivation, water percolation of 10 mm per day was carried out in lots 2, 4, 5 and 6, but not in lots 1 and 3. In the 1st lot (no lime, no percolation) the pH was 2.6~3.3 and rice plants could hardly grow in 1959~1962, but grew well in 1963. The

Table 1. Soluble Al, Fe and Mn Contents of Shimata Soil (mg/100g)

Date	Sample Horizon	pH	Water soluble			KCl soluble	
			$\text{Al}^{3+}$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{Al}^{3+}$	$\text{Fe}^{2+}$
1960	May {	0~1.5cm	23.1	21.3	9.4	94.0	10.4
		1.5~10	29.1	24.1	16.4	50.3	1.1
	July	0~12	33.9	13.7	10.4	91.9	3.2
1964	June {	0~12	1.1	0.8	0.2	112.2	7.7
		12~22	37.0	64.8	12.5	103.1	7.0

Note: Oxidizable sulfur before oxidation: 22mg/g soil, Soil: Heavy Clay

Table 2. Yield of Lysimeter Experiment (brown rice kg/a)

Treatment	1958	1959	1960	1961	1962	1963
1. No lime, no percolation	—	0	0	1.5	1.9	75.5
2. No lime, percolation	—	4.5	9.3	38.6	69.7	64.7
3. Lime, no percolation	—	22.5	53.1	37.1	76.8	63.0
4. Lime, percolation	—	33.6	61.6	54.0	80.2	71.0
5. Lime, percolation, after 3 years upland condition	—	—	—	72.4	74.1	75.0
6. Flooding, percolation a whole year	28.5	61.6	78.2	52.4	70.8	63.0

Note: Soil used is the bottom mud of the Bay of Iya. Lots 1-5 were manured since 1962. Lot 6 was manured only with N in 1959~1961 and the same amounts of N, P and K as lots 1-5 since 1962.

**Table 3. Some Chemical Characters of Lysimeter Soils (Nov. 1961)**

Treatment	pH	C %	N %	Oxidizable S mg/g	H <sub>2</sub> O solu. SO <sub>4</sub> -S mg/100g	HCl solu. Fe <sub>2</sub> O <sub>3</sub> %	free Fe <sub>2</sub> O <sub>3</sub> %	HCl solu. MnO <sub>2</sub> mg/100g
1. No lime, no percolation	3.5	1.29	0.17	1.6	0.3	4.84	1.88	38
4. Lime, percolation	6.5	1.40	0.14	2.4	2.1	4.68	1.71	40
6. Flooding, percolation a whole year	5.9	3.31	0.19	21.3	0.4	2.28	1.05	70

growth, however, was unstable in the following years, showing wide fluctuations.

The good effects of liming and percolation were evident. The yield was highest in the 4th and 5th lots where both treatments were carried out, while it was lower in the unacidified soil where the water content was higher, physical conditions were inferior and tilling was very hard. Differences in content of the main soil components among the lots in the fourth year are shown in Table 3.

This table shows that there is nearly no oxidizable sulfur remaining in the acidified soil (lots 1~5). A decrease in amount of organic carbon and HCl soluble Mn, and an increase of HCl soluble and free iron are also noticed in this soil. Iron liberated from FeS<sub>2</sub> by oxidation is oxidized and precipitated, increasing in the soil. SO<sub>4</sub> is decreased by leaching. Mn is strikingly leached in the acidified soil.

In the unacidified soil oxidizable sulfur remains as it is, being in danger of acidification in future. This soil also contains much easily decomposable organic matter and a little free iron. And reduced condition develops in this soil owing to the whole year flooding, often doing damage to rice plants.

The yields of rice in another experiment carried out in the pots using the same soil and no percolation during rice cropping are shown in Table 4. In this case the unacidified soil (in the whole year flooded condition) became strongly reduced condition owing to application of compost and caused damage to rice plants, while in the acidified soil (drained during the period of the second dropping) application of compost at first caused a little damage to rice plants, but produced good results later on.

**Table 4. Yield Index in Pot Experiment**

Treatment	Unacidified soil, average of 3 years	Acidified soil	
		1961	1963
O	14.7	39.7	31.6
P K	16.1	45.4	23.7
N K	62.9	89.9	82.2
N P	94.4	97.8	98.8
N P K	100.0	100.0	100.0
NPK, compost	21.2	89.6	119.0
Rough rice weight per pot in NPK lot	43.5g	67.2g	68.7g

In this lysimeter experiment, the amount of lime applied was 50, 56, and 24 ton per ha, respectively, in lots 3, 4 and 5 in Table 2. The amount of lime can be saved in case the soil is treated to promote the oxidation of oxidizable sulfur and the sulfate produced are washed away by rain or irrigation before the application.

The analysis of rice straw in the ripening period in 1961 showed that P was lower, and Fe, S and Al were higher in content in lot 1 (no lime, no percolation). By the percolation P was increased and Al was decreased. Fe, S and Al were decreased by the application of lime without percolation, but P was not increased in this case. In case liming is accompanied by percolation P was increased, and Fe, S and Al were decreased. Al<sup>3+</sup> decreased remarkably, Fe<sup>2+</sup> decreased fairly and free H<sub>2</sub>SO<sub>4</sub> disappeared in the soil solution after liming.

Percolation without liming also has a similar effect though it takes a longer time to be effective. Liming accompanied by percolation has an additional effect of decreasing Fe<sup>2+</sup> remarkably. It seems that the damage of the growth of rice plants in the acid sulfate soil

is due to the direct effect of  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ , and also to an indirect effect of them causing deficiency of phosphorus.

In addition to those, the damage by  $\text{Fe}^{2+}$  is heavier in case the pH is lower. Kobayashi<sup>1)</sup> reported that the existence of free  $\text{H}_2\text{SO}_4$  increased the damage in the acid sulfate soil. Tanaka<sup>3)</sup> said that the inferior growth of rice plants in the acid sulfate soil was mainly due to damage by iron, and could be improved by liming or application of much phosphate. In the field, furthermore, the effect of water percolation can not be neglected as it is difficult to improve subsoil.

It is recommended for the cultivation of rice plants in the acid sulfate soil to make lower the level of underground water and improve percolation by open or underdrain, and to promote the oxidation of sulfur, washing away the injurious products by rain and irrigation. Rice plants are cultivated there after liming and flooding. Much phosphate is applied and water percolation is continued throughout the cultivating period.

### On the upland crops

It is more important for upland crops than for rice crops to promote the oxidation of sulfur at first and to wash away injurious components. Tilling is effective for promoting the oxidation of sulfur. Deficiency of phosphorus is especially apt to occur in the acid sulfate soil of upland farms. It was observed in the pot experiment that nearly all the phosphorus of the Ca- and Al-types contained in the original soil and much of the phosphorus applied as fertilizers have changed into that of the Fe-type four years after.<sup>9)</sup> This change is due to the production of a large quantity of active iron by oxidation of pyrites. Accordingly, the yield index of wheat in the lot of no phosphorus was only 17 in this experiment. In addition to liming application of much phosphorus is especially needed in upland farms.

The cultivation of rice plants is comparatively easy in the acid sulfate soil in case the

field can sufficiently be irrigated and drained. In an upland farm of acid sulfate soil the effective soil is shallower because of a difficulty in improving the subsoil. Consequently, the crops are often damaged by a drought in case it rains little in summer. Improvement of the subsoil and irrigation of upland farms are problems to be studied in future.

### References

- 1) Kobayashi, T.: Ibaragi Agr. Exp. Sta., Rinji Hokoku No. 3, 1-47, 1938.
- 2) Yoneda, S.: Genetic and Edaphologic Studies of the Polder Soils in Japan. Report of the Laboratory of Soils and Fertilizers, the Faculty of Agriculture, Okayama University, No. 8, 1-183, 1964.
- 3) Tanaka, A. and S. A. Navasero: Growth of the Rice Plant on Acid Sulfate Soils. *Soil Sci. and Plant Nutrition*, 12, 107-114, 1966.
- 4) Murakami, H.: Distribution and Characteristics of Acid Sulphate Soils in the Region of Lake Nakaumi and Shinji, Characteristics and Improvement of Acid Sulphate Soils (I). *J. Sci. Soil Manure, Japan*, 38, 112-116, 1967.
- 5) Murakami, H.: On the Forms of Oxidizable Sulphur, Characteristics and Improvement of Acid Sulphate Soils (II). *J. Sci. Soil Manure, Japan*, 38, 117-120, 1967.
- 6) Sugawara, K., Koyama, T. and Kozawa, A.: Distribution of Various Forms of Sulphur in Lake, River, and Sea-Muds (II). *J. Earth Sci., Nagoya Univ.*, 2, 1-4, 1954.
- 7) Kanno, I., Honjo, Y., Arimura, S. and Tokudome, S.: Genesis and Characteristics of Rice Soils Developed on Polder Lands of the Shiroishi Area, Kyushu. *Soil Sci. and Plant Nutrition*, 10, 1-19, 1964.
- 8) Murakami, H.: A Method of Semi-quantitative Determination of Oxidizable Sulfur in Polder Soils by Hydrogen Peroxide. *J. Sci. Soil Manure, Japan*, 32, 276-279, 1961.
- 9) Murakami, H.: Behaviour of Mineral Components of Acid Sulphate Soils During the Oxidation of Oxidizable Sulphur, Characteristics and Improvement of Acid Sulphate Soils (IV). *J. Sci. Soil Manure, Japan*, 39, 194-198, 1968.
- 10) Murakami, H.: Effect of Sulphur Oxidation on Soil Chemical Nature and Rice Plant Growth, Characteristics and Improvement of Acid Sulphate Soils (V). *J. Sci. Soil Manure, Japan*, 39, 514-519, 1968.