Effects of pH and Redox Conditon on Silica Sorption in Submerged soils

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湛水條件에서 土壤酸度와 酸化還元 電位가 土壤의 珪酸吸着에 미치는 影響

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SUMMARY

Silica sorption isotherm belonged to the C-type with weak L-type characteristics according to the classification system of adsorption isotherm. Silica sorption isothem fitted well to the Freundlich and Tempkin equation but not to the Langmuir equation. The color interference probably due to Fe^{2+} during spectrometric silca determination by Molybdenum-blue method affected the sorption isotherm in reduced soils or low pH.

Four parameters such as the intercept of Freundlich equation, the slope of Tempkin equation, the "Silica reactivity", and the "C-type slope", where the last two parameters were termed in the current study, were examined to assess treatment effects on silica sorption. Among them the "C-type slope" was found out to be the best parameter. The C-type isotherms showed the same high correlation coefficient as Freundlich and Tempkin equation when regressed to the sorption isothem. Plotting the C-type slope on a logarithmic scale vs. the pH showed high linearity.

Using the "C-type slope" as a perameter, the pH and soil type affected the silica sorption while the effect of redox condtion was not significant.

All Fe and Al extracted by the various reagents, and OM were highly correlated to silica sorption. Among them Fe_d was identified as the highest influencing soil property. Since there is no equivalent reliable method to discriminate the forms of the soil Al-oxides their likely importance remains unclear.

INTRODUCTION

Sillica is beneficial for the development of rice plants and may be considered as a nutrient element to the plants from an agronomic view point, though the physiological essentiality is not well established. Silica has been reported to benefit rice plants in maintaining erect leaves, improving resistance to disease and insects, and in regulating osmosis[30].

The optimum silica level in top soil extracted by 1N sodium acetate at pH 4 is 130 ppm as SiO_2 for Korean soils[28]. About 90% of Korean paddy soils are considered to be deficient in silica, since they are low in clay content which is the major source of available silica. Therefore, silica is considered to be one of the most important element for rice production in Korea.

Sorption-desorption reactions of sesquioxides and clay minerals are faster in Si equilibrium than dissolution-precipitation phenomena[3, 4, 19, 24]. Mckeague and Cline[24] reported that freshly precipitated hyd-

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roxides of polyvalent metal ions were more effective, some soil samples and iron oxide minerals were moderately effective, and alkaline-earth carbonate minerals were ineffective in adsorbing dissolved silica.

Silica adsorption is pH dependent. Adsorption increases to a maximum at pH 9.2 and decreases with further pH increase[3, 17, 18, 24].

The silica chemistry in flooded soils is not well understood. Silica is not involved in oxidation-reduction reaction but flooding influences its behavior in paddy soils. Silica concentration tends to increase in paddy soils after submergence due to release of adsorbed and occluded silica in Fe(III) oxyhydroxides[29, 32]. Flooding of soils not previously flooded, however, results in a decrease in soluble Si^{21}. Yoon and Hwang[47] reported the increased adsorption of Si by reduced soils with increase of amorphous Fe oxide minerals.

The silica behavior in flooded soil is affected by pH, kinds and amounts of clay minerals, and their transformation in different conditions such as Eh and electrolyte levels, and competitive reaction with other ligands such as boron[14] and phosphorus[9]. Flooding may change these factors with close interrelationship between each other[32]. Therefore, seperate evaluation of the effects of those factors on silica sorption is required.

Standard methods to estimate application effects of various silicate materials has not been established well due to the complexity of impurities and their different reactions in submerged soils[26]. Recently, new method to estimate available silica for rice plant by incubating the soil with water for one week and analyzing the silica content in soil solution was proposed because extracting Si with sodium acetate solution is not very reliable[40].

More baseline studies on silica in submerged soils are required to solve these problems. The objectives of this study are (1) to determine the effect of pH, redox condtion, and types of soil on

silica sorption and (2) to identify soil properties that mainly control Si sorption.

MATERIALS AND METHODS

Soil samples

The soil samples at 0 to 20 cm depth of two philippine soils and two Korean soils were used in the study. The soils used were : Luisiana(Clayey, halloysitic, isohyperthermic Palehumult) ; Maahas(Fine, mixed, isohyperthermic typic Tropudalf) ; Yongji(Fine-loamy, Aquic Fluventic Eutrocrepts) ; Mangyeong(Coarse−silty, Fluventic Haplaquepts). Selected chemical and physical properties of these soils are shown in Table 1.

Standard methods were used to determine the properties listed in Table 1, Clay percentage was determined by the pipette method, organic carbon by the method of Walkley and Black[6], soil pH in a 1 : 2 soil/water suspension, CEC by saturation with pH 7 ammonium acetate and displacement of

Table 1. Selected chemical and physical properties of the soils used in the experiments.

Soil properties	SOIL			
	Luisiana clay	Maahas clay	Yongji loam	Mangyeong silty loam
Clay contents(%)	73	68	26	10
CEC (me/100g)	21.1	44.3	9.78	7.15
pH (1 : 2)	4.5	6.6	4.9	5.6
Org. C (%)	2.66	1.53	1.43	0.65
Exch. Fe (me/100g)	0.05	0.052	0.072	0.052
Fe_p (%)+	0.93	0.31	0.43	0.091
Fe_o (%)	1.12	0.72	0.59	0.26
Fe_d (%)	2.03	0.71	0.82	0.25
Exch. Al (me/100g)	1.5	0.022	0.61	0.056
Al_p (%)	0.54	0.11	0.22	0.017
Al_o (%)	0.62	0.21	0.26	0.067
Al_d (%)	0.50	0.039	0.15	0.024

+ Subscript p, o, and d denotes "pyrophosphate extractable", "acid oxalate extractable", and "dithionite-citrate extractable", respectively.

adsorbed ammonium with acidified NaCl[6], exchangeable Fe and Al by extraction with potassium chloride, pyrophosphate extractable Fe and Al by extraction with 0.1M sodium pyrophosphate at pH 10 for 16 hours[23], oxalate extractable Fe and Al by extraction with 0.2M ammonium oxalate/oxalic acid solution at pH 3 by 4 hours shaking in the darkness[25], Dithionite-citrate extractable Fe by extraction with concentrated dithionite-citrate reagent by 16 hours shaking at room temperature[7].

Pretreatment of Soil Samples

The pretreatment of the soils was conducted to get steady state conditions of oxidized and reduced soils for further study as follows.

The 1.25 kg of soil samples were submerged in 0.01M $CaCl_2$ solution at a soil-to-solution ratio of 1 : 2 in wide mouth 4 liter plastic containers. The containers were tightly covered to air-proof with No. 14 rubber stoppers and equipped with two platinum electrodes and one glass tubes immersed in the soil suspension as gas inlet and another glass tube above the soil suspension as gas outlet. A 1cm diameter hole for pH determination and sampling was also made on the rubber stopper and covered tightly to air-proof with No. 1 rubber stopper. The bulk soil suspensions were placed in a water bath and kept at room temperature. For one hour every 2 days upto 3 months the samples were purged with CO_2-free N_2 or O_2 gas. This treatment ensured the steady state with constant pH and Eh level. Before each gas purging pH and Eh of soil suspension was determined after mixing the suspension completely.

Sorption Study

After steady state was reached, five ml subsamples were taken from the bulk soil suspension using automatic pipette during stirring the bulk soil suspension vigorously and purging N_2 or O_2 gas. The samples were put into centrifuge tubes containing 15 ml of triplicate series of SiO_2 solution (0, 20, 40, 80, 100, 120 mg SiO_2/L) in 0.1M NaCl. One ml of various predetermined concentrations of NaOH or HCl solution were added to the suspension to adjust the pH to 4 levels (pH 5, 6, 7, and 8). Oven dry weights of soils were also determined. The centrifuge tubes were tightly sealed with Suba-seal and purged with N_2 or O_2 gas for 20 minutes to replace the air inside using spinal needles with its tip immersed into the soil suspensions. Thereafter the samples were shaken for 4 hours in a 25℃ waterbath and centrifuged. The supernatant was immediately analyzed for pH and filtered with No. 42 Watmann filter paper. The filtrate was analyzed for Si using the molybdenum-blue method[22]. The difference between the Si concentration in the initial solution and supernatant was considered as being sorbed by the soil.

The Langmuir, Freundlich, and Tempkin equation were used to interpret the equilibrium sorption data. The linear form of Langmuir equation is

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where C is the equilibrium SiO_2 concentration, x/m is the amount of SiO_2 sorbed per unit mass of adsorbent, b is the SiO_2 sorption maximum, and k is a constant related to the energy of adorption.

The Freundlich equation is

$$x = k \, C^b \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where k and b are coefficients. The fit of sorption data to Freundlich equation is determined by the linearity of the plot of log x vs. log C. This equation corresponds to a model of adsorption in which the affinity term decreases exponentially as the amount of adsorption increases[16].

The Tempkin equation is

$$x = k_1 \, \ln \, (k_2 C) \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

where k_1 and k_2 are coefficients. This equation describes data best if adsorption plotted against log concentration gives a straight line. The model of adsorption is based on a linear decrease of the affinity term as the amount of adsorption increases[16].

The direct linear regression of sorption isotherms was conducted to establish another parameter for interpreting the sorption data. Following the classification system of sorption isotherm[12], the slope of the linear regerssion is named "C-type slope" in this study

The "Silica reactivity" named in this study is a modification of the "Index of Silica Reactivity" proposed by Gallez et al.[11] was also determined in the experiment. The "Silica reactivity" is defined as the percentage of soluble silica lost from initial 100 ppm SiO_2 solution after equilibrium at a certain pH level.

pH_O Measurement by Potentiometric Titration Method

The methods of Gillman and Uehara[13] were used. Seven ml samples of soil suspension were taken during vigorous mixing of bulk soil suspension and put in 50 ml centrifuge bottles. The samples were washed with 20 ml 1M NaCl solution by shaking and centrifuging to get the samples free of exchangeable cations and anions and further washed with distilled water until the electrolyte concentration reduced to a low value (Ex. 0. 002M). Then, 20 ml of 0.002M NaCl solution was added to each of the centrifuge tubes. After adding one ml NaOH or HCl solution of varying concentrations for the whole pH range the samples were shaken overnight. The equilibrium pH ($pH_{0.002M}$) were recorded. Then, after adding 0.5 ml of 2M NaCl and gently shaking for about 3 hours in an end-to-end reciprocating shaker, the pH ($pH_{0.05M}$) was recorded. In each centrifuge tubes $\triangle pH = (pH_{0.05M} - pH_{0.002M})$ was calculated and

$\triangle pH$ vs. $pH_{0.002M}$ was plotted.

The pH_O is the $pH_{0.002M}$ showing $\triangle pH = 0$ by extrapolating. The pH_O is independent of salt concentration, and is the zero point of charge resulting from the variable charge component.

Surface Charge Measurement By Cation and Anion Exchange Methods

Positive and negative charges in soil were determined measuring cation and anion retention according to Schofield[35] as described by van Raij and Peech[42].

Seven ml of soil suspension subsamples were taken during vigorous mixing of bulk soil suspension, placed in 50 ml centrifuge tubes, and saturated with 20 ml 1M NaCl solution. The water content of soil was determined. After being shaken for 1 hour, centrifuged and decanted, the soil suspensions were washed 3 times with 0.2 M NaCl solution, and centrifuged 5 times with 0.1M NaCl solution. After the washing treatment 20 ml 0.1 M NaCl and One ml NaOH or HCl solution with varing concentrations were added and the samples were shaken overnight. Each concentration was done in triplicate. After centrifuge the pH of supernatant solution was recorded. Immediately after discarding the supernatant solution the centrifuge bottles were weighed to obtain correction for entrapped Na^+ and Cl^-. Finally the Na^+ and Cl^- were extracted 5 times with 20 ml of 0.5M NH_4NO_3 solution. Na^+ was analyzed by atomic adsorption spectrophotometer. Cl^- was analyzed potentiometrically with a chloride ion specific electrode (Orion ionanalyzer Model 94−17).

RESULTS AND DISCUSSION

Changes in Soil Chemical Properties Under Reduced and Oxidized Conditions

The pH of the aerobically incubated soils did not change much form the original pH. Variation

was at most 0.5 pH (Fig. 1). The pH of the incubated soil under reduced condition increased asymtotically to pH 6.9 in Maahas and Mangyeong soils and pH 6.3 in Luisiana and Yongji soils. mangyeong soil reached the steady state after 20 days of incubation, Maahas and Yongji soils after 1 month, and Luisiana soil after two months.

The Eh of oxidized soil decreased during the first 10 days and then increased continuously up to 700 and 450 mV in Yongji and Mangyeong soil, respectively. The Eh of Luisiana soil decreased and reached a steady state at 350 mV whereas Maahas soil maintained more or less same Eh level of 300 mV throughout the incubation period. The Eh of reduced soils decreased asymtotically

reaching a steady state after about 1 to 2 months incubation depending on the soils (Fig. 2). The Eh at steady state was around -180 mV in Yongji and Mangyeong soil, -100 mV in Luisiana soil, and 0 mV in Maahas soil.

The change of soil chemical properties of dried soils after 3 months incubation under oxidized and reduced conditon are shown in Table 2. The available SiO_2 contents extracted by 1N sodium acetate buffer solution of pH 4 increased much in reduced soils but remained unchanged in oxidized soils. Maahas soil yielded more than 1,000 ppm, which is much above the optimum level of 130 ppm[28].

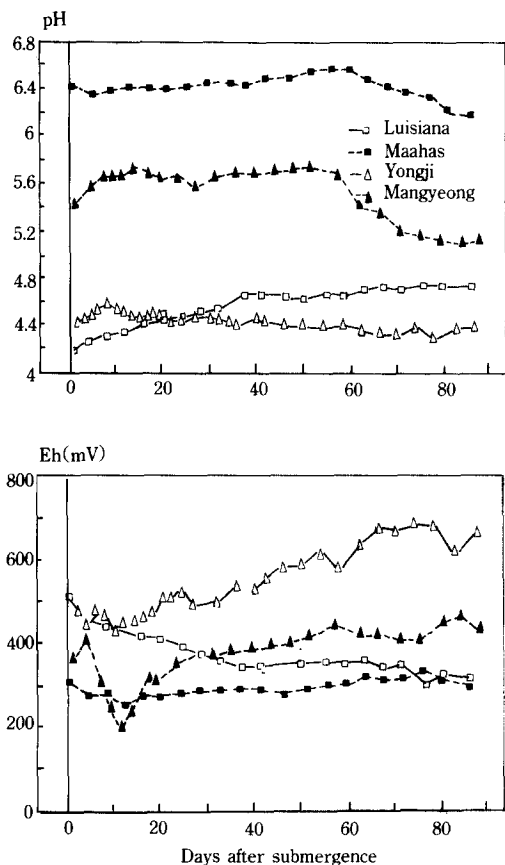Yoon and Hwang(1984) reported that the avai-

Fig 1. Kinetics of soil suspension pH and Eh of various soilss during incubation under *oxidized condition*
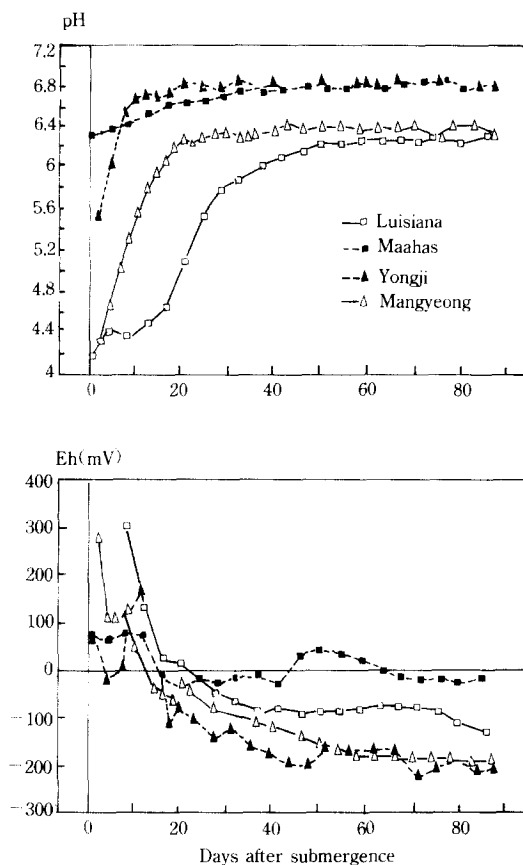

Fig 2. Kinetics of soil suspension pH and Eh of various soils during incubation under *reduced condtion.*

Table 2. Changes of chemical properties of dried soils after incubation under oxidized and reduced condition.

SOIL	INCUBATED CONDITION[++]	pH (1:1)	OM	Fe_p[+]	Fe_o	Fe_d %	Al_p	Al_o	Al_d	Olsen P	Avail SiO_2 ····· ppm ·····	Exchangeable Fe	Al ····· me/100g ·····
Luisiana	In.	4.5	5.8	0.93	1.12	2.03	0.54	0.62	0.50	5	219	0.05	1.5
	Ox.	4.5	5.2	0.87	1.16	2.36	0.41	0.63	0.52	5	262	0.16	0.53
	Red.	4.8	5.4	0.84	1.44	2.10	0.41	0.68	0.47	2	394	0.18	0.11
Maahas	In.	6.6	2.7	0.31	0.72	0.71	0.11	0.21	0.039	9	1037	0.052	0.022
	Ox.	6.5	2.9	0.38	0.74	0.76	0.11	0.22	0.046	11	1094	0.050	0.022
	Red.	7.4	2.8	0.41	0.83	0.75	0.10	0.24	0.048	13	1106	0.056	0.016
Yongji	In.	4.9	2.6	043	0.59	0.82	0.22	0.26	0.15	3	131	0.072	0.61
	Ox.	4.5	2.5	0.38	0.56	0.8	0.20	0.24	0.15	3	124	0.072	0.44
	Red.	4.8	2.3	0.43	0.62	0.91	0.21	0.27	0.17	2	221	0.14	0.19
Mangyeong	In.	5.6	0.5	0.091	0.26	0.25	0.017	0.067	0.024	20	128	0.052	0.056
	Ox.	5.5	0.8	0.089	0.28	0.27	0.017	0.091	0.026	22	134	0.057	0.037
	Red.	6.3	0.5	0.067	0.23	0.20	0.012	0.073	0.023	14	174	0.048	0.022

[+] Subscript p, o, and d denotes "pyrophosphate extractable", "acid oxalate extractable", and "dithionite-citrate extractable", respectively.
[++] In. = Initial, Ox. = Oxidized condtion, Red. = Reduced condition.

lable silica in the submerged soil increased as pH went up to neutral condition and Eh decreased.

Dithionite-citrate extractable Fe, designated as Fe_d, and acid oxalate extractable Fe, designated as Fe_o has been commonly used to estimate the contents of total free iron oxide and amorphous iron oxide in the soil, respectively[43]. No specific extraction method has been developed to discriminate Al oxides[41]. Thus the extracting reagents for Fe oxide mineral have been commonly used for extracting Al oxide mineral[27].

Fe_o increased upon reduction in all soils but did not change in the oxidized treatment except in Mangyeong soil which showed low Fe_d. Quantitative estimates of crystalline Fe in goethite and hematite could be made form Fe_d-Fe_o[27].

During early stage of reduction Fe oxides possibly were dissolved[45]. Upon prolonged flooding the Fe(II) compounds might be precipitated[32]. In flooded soils up to 83% of the Fe(II) occurs as precipitates and only a small fraction were pre-

sent as dissolved Fe^{2+2}. Therefore, the increase of Fe_o in reduced soils seemed to be due to the precipitation of non-crystalline Fe compounds, possibly Fe(II) compounds.

Fe_d was higher than Fe_o in Luisiana and Yongji soils, whereas they were similar in Maahas and Mangyeong soils. Fe_d>Fe_o results form the presence of pedogenic crystalline iron oxide minerals which do not dissolve in oxalate reagent when light is excluded, but dissolve in dithionite reagent [27]. Therefore, similar values of Fe_o and Fe_d imply that amorphous Fe is the predominant oxide mineral in those soils.

In all soils the Al_o was greater than Al_d. In Maahas soil which contained high allophanic minerals, this was consistent with the observation that oxalate might be more efficient in extracting Al from allophane than dithionite-citrate, which usually dissolves only about 25% of the Al in allophanes[10]. These results confirm that forms of Al can't be clearly identified by these reagents.

The surface charge characteristics at various pH of the soils were shown in Fig. 3. The induced adsorption of Na^+ and Cl^- on the soil surface reflects the positive and negative charges of the soils, respectively. All the soils showed predominant negative charge and only small positive charge. The negative charge increased with increasing pH. The amount of negative charge at any pH level in various soils were proportional to the CEC which is the negative charge determined at pH 7. At pH 3 to 5 the negative charge decresed and the positive charge increased in reduced soils raising slightly the zero point of net charge compared with the oxidized soils. The increase in Fe_o

due to reduction (Table 2) probably raised the zero point of net charge by increasing the number of reaction sites. Amorphous Fe oxide has higher surface area and reaction sites than crystalline Fe oxide.

The zero point charge of the variable charge component, designated as pH_o, increased in reduced soils by 0.7 and 1.0 pH unit in Luisiana and Mangyeong soil, respectively (Fig. 4). Other soils showed same tendency. Similar to the change of zero point of net charge, probably the increase of Fe_o in reduced soils increased the pH_o
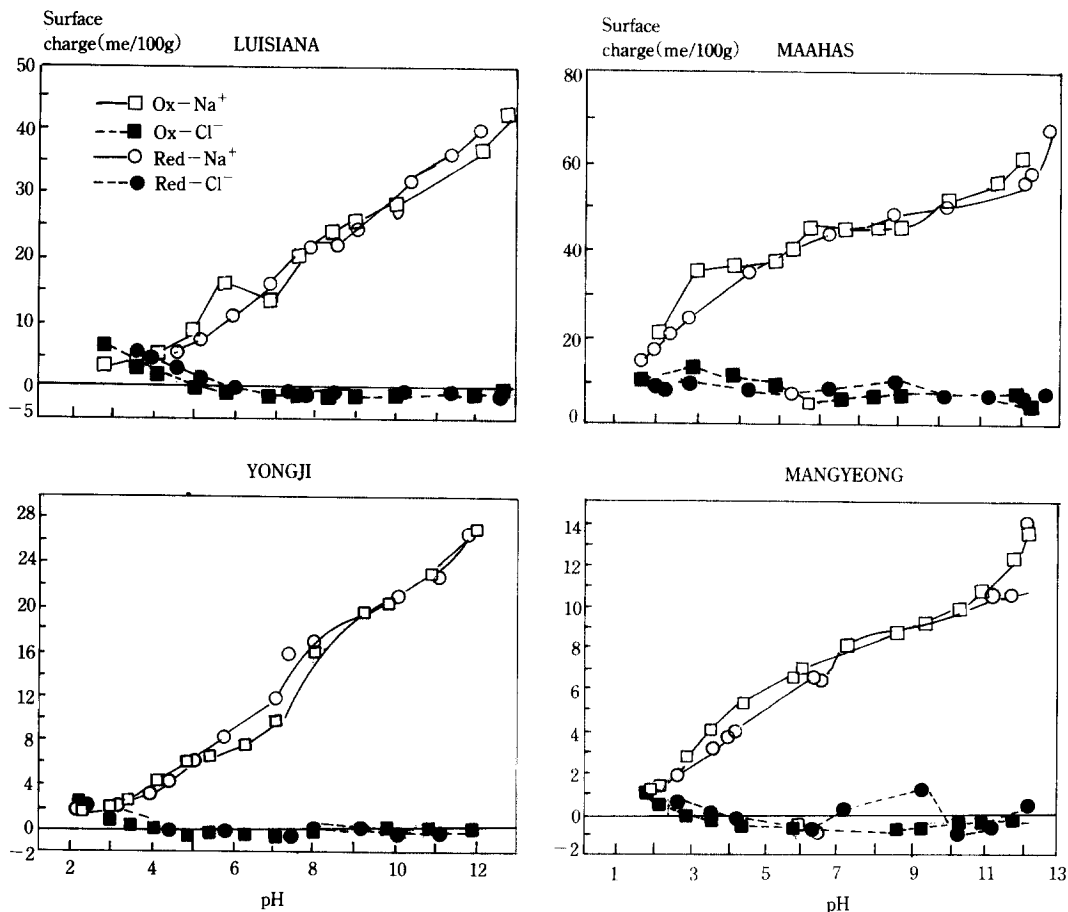
Silica Sorption Study

Fig 3. **Surface charge characteristics at a range of pH in various soils incubated under oxidized or reduced condtion. Ox- and Red- desingnate oxidized and redued incubating condtion ; -Na$^+$ and -Cl$^-$ designate absorbed Na$^-$ and Cl$^-$ by the soils.**
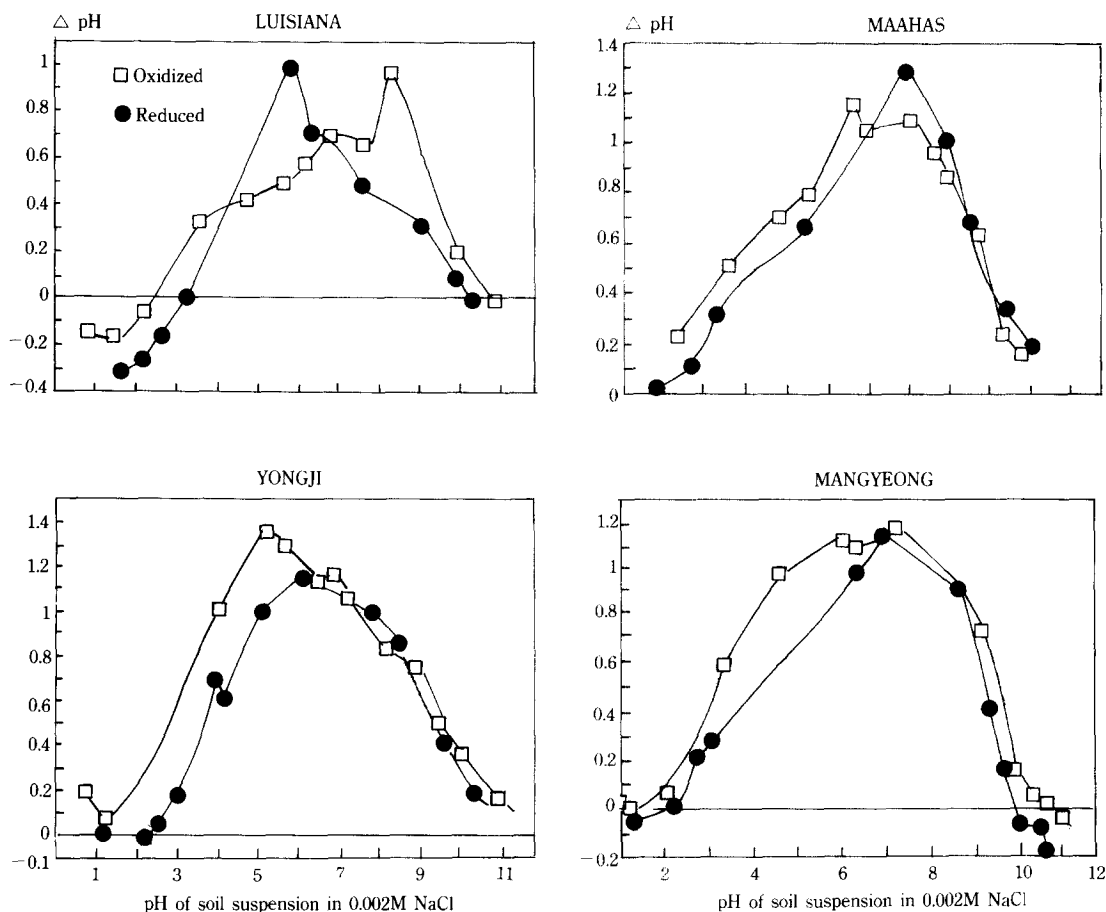
Fig 4. △pH at various soils incubated under oxidized and reduced condition.
$\triangle pH = pH_{0.05M\ NaCl} - pH_{0.002M\ NaCl}$.

Silica sorption isotherms describing the relationship between the amount of sorbed Si and its bulk phase concentration at given temperature, showed C-type isotherm having weak L-type according to the classification system of Giles et al[12] (Fig. 5). It has been reported that Si/goethite is a type L, subclass "c" isotherm. The subclass "c" classification implies that the sorption does not approach a fixed value (Miller et al., 1984a). A C-type adsorption is consistent with models whereby the extent of adsorbing surface is inc-into and is adsorbed within the adsorbent[15]. The slope at each point of adsorption isotherm indicates the ease with which the adsorptive species

can bind to the surface[15].

Silica sorption isotherm was well fitted to the Freundlich and Tempkim equation but not to the Langmuir equation (Fig. 6).

The determination of the Si sorption isotherm curve may have been hampered by a color change during spectrometric Si determination using molybdenum-blue method (Fig. 7). A blue green color development instead of pure blue color was observed. The color change was apparent in reduced Maahas soil and in other reduced soils of low pH level, pH 5. the lower the pH in Maahas soil the more the color changed to blue green. It has been reported that Fe^{2+} interferes color de-
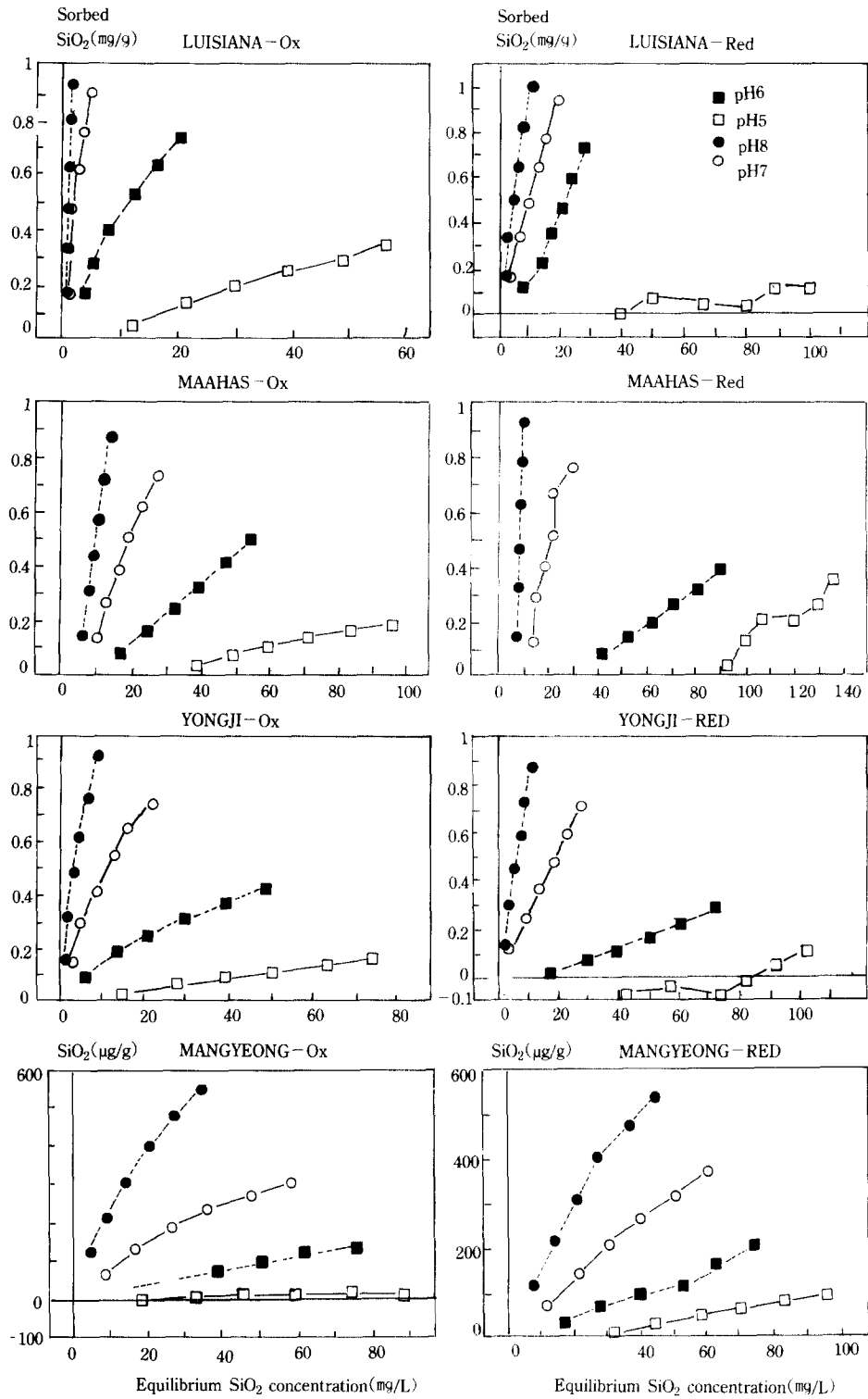
Fig 5. Silica sorption isotherm at four pH levels in various soils incubated under oxidized or reduced condition.
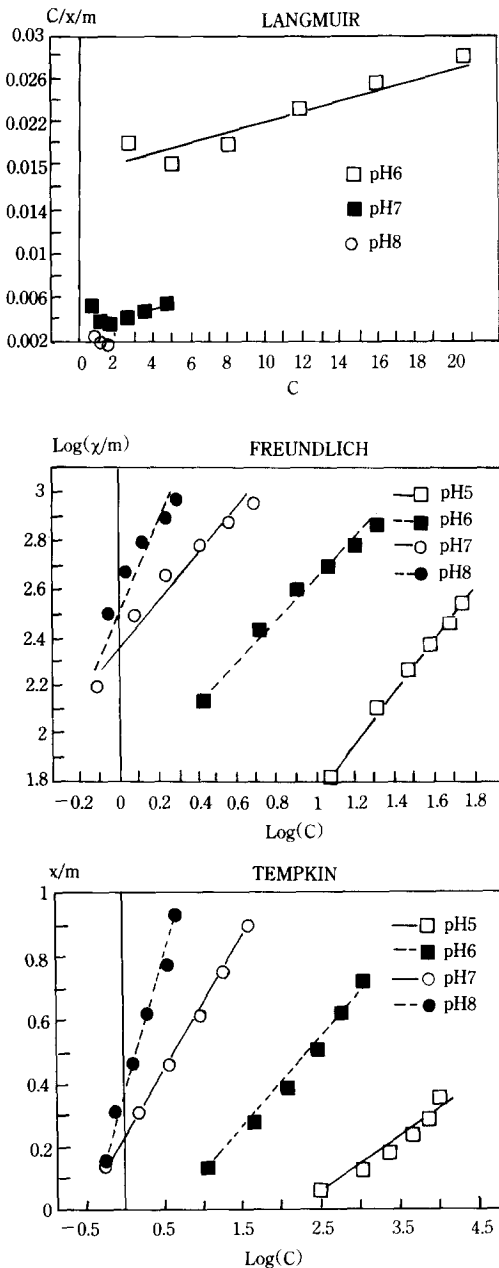
Fig 6. Langmuir, Freundlich and Tempkin isotherm for silica sorption by Luisiana soil incubated under oxidized condition. x=μg SiO₂, m=g soil, C=mg SiO₂/L of equilibrium solution.
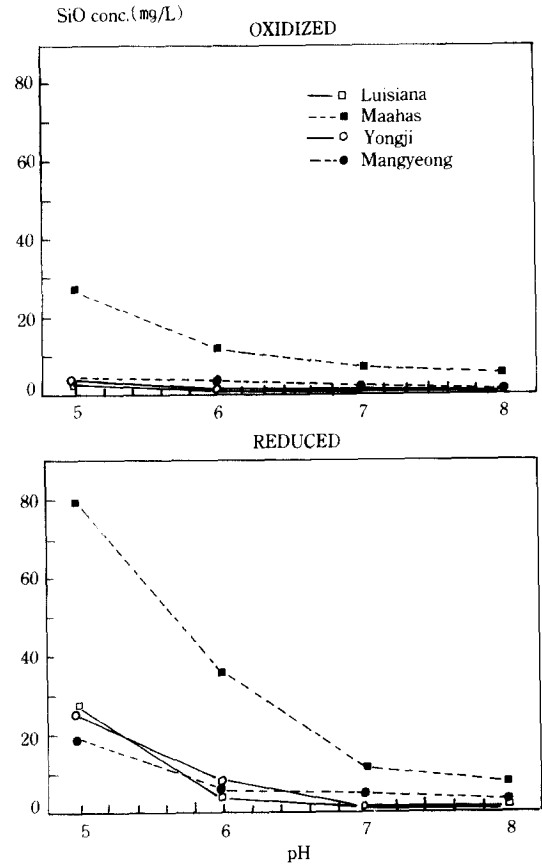

Fig 7. pH-dependent color inhibition occuring in spectrometric determination of silica content in various soils incubated under oxidized or reduced condition with molybdenum blue method.

velopment by premature reduction of the molybdophosphoric acid when P is present[44]. Sumida and Ohyama[38] have reported that Fe^{2+} under re-

duced condition interferes with color development resulting in overestimation of the Si content. They recommended the use of ion-exchange resin for the removal of Fe^{2-} before color development.

Because of the color interference the available Si contents extracted at pH 4.0 with 1N sodium acetate buffer solution were always incorrectly higher in reduced than in oxidized soils (Table 2). The available Si contents extracted with above solution is used as a standard method for the diagnosis of Si fertility of the soils in Korea and Japan[22]. However, the method has been criticized because the measured Si content of soils applied with Si fertilizer were poorly correlated to Si ab-

sorbed by the plants[39]. The application of this method to diagnose Si fertility in flooded rice soils has to be reevaluated.

For the assessment of treatment effects the most proper parmeter has to be chosen in the frist step. For the purpose four parameters such as the "Silica reactivity", the intercept of Freundlich equation, the slope of Tempkin equation, and the "C-type Slope" were examined to evaluate the effects of pH, redox condition, and soil properties on Si sorption.

The "Silica reactivity" termed in the present study is the percentage of sorbed silica lost from the initial solution. The coefficients of Freundlich and Tempkin equation were used as parameters because they well described the silica sorption isotherm (Fig. 6). Based on the observation that sorption isotherm showed a strong C-type (Fig. 5). The slope in simple regression of the sorption isotherm is introduced as describing parameter. Accordingly, this parameter will be called "C-type slope" in this study. The coefficients of determination of the C-type slope in linear regression analysis was similarly high as those of Freundlich and Tempkin equations (Table 3).

The statistical analysis of treatment effects using the "Silica reactivity" and the "C-type slope" corresponded well with the sorption isotherm. There was no effect of redox condition on Si sorption whereas the effect of pH and soil type was highly significant (Table 4).

Using the "C-type slope" as a parameter, the silica sorption increased with increase of pH (Table 5). The soil types strongly affected the silica sorption following the order Luisiana〉Maahas=Yongji〉Mangyeong (Table 6). The same results, not seen in this paper, were obtained by using the "Silica reactivity" as a parameter.

On the other hand the effect of redox condition on silica sorption was overestimated by the intercept of Freundlich equation and underestimated

Table 3. Comparison of coefficients of determination among various isothermal equations.

TREATMENT		ISOTHERMAL EQUATION[+]		
Kinds of soil	Redox Condition	Freundlich	Tempkin	C-type
Luisiana	Oxidized	0.963	0.984	0.973
	Reduced	0.985	0.961	0.994
Maahas	Oxidized	0.965	0.994	0.993
	Reduced	0.878	0.951	0.952
Yongji	Oxidized	0.983	0.976	0.975
	Reduced	0.987	0.967	0.994
Mangyeong	Oxidized	0.902	0.936	0.921
	Reduced	0.985	0.966	0.983
Average		0.956a[+ +]	0.967 a	0.973 a

[+] Freundlich = Freundlich isothermal equation (Eq. [2]) ; Tempkin = Tempkin isothermal equation (Eq. [3]) ; C-type is a direct linear regression to silica sorption isotherm.

[+ +] Numbers in a row with the same letter are not significantly different by paired t-test.

by the slope of Tempkin equation, while the effects of pH and soil types was consistent with the results obtained by the "Silica reactivity" and the "C-type slope".

The Freundlich equation is thought to be strictly an empirical expression without chemical significance though it often highly correlates with adsorption data obtained at constant temperature. However, it is capable of rigorous theoretical derivation of P sorption[37]. The intercept of the equation may be considered as a hypothetical indices of P adsorbed from a solution having a unit equilibrium concentration, and may thus be taken to provide a measure of relative P sorption capacity of different soils[5]. Meaningful comparisons of different soils on this basis could be made[8]. On the other hand, the slope of the equation is clearly a measure of P buffering capacity when it is expressed in logarithmic terms[31] The value of the slope has been reported not to be affected by

Table 4. F-value in the analysis of variance for four parameters to determine the effect of pH and redox condition on silica sorption.

SV[+]	DF	KINDS OF PARAMETER[++]			
		Silica reactivity	C-type[+++] slope	Freundlich intercept	Tempkin slope
Block	3	44.10**	62.98**	5.81**	48.18**
Treatment	5	24.87**	32.00**	2.86ns	14.52**
Redox (r)	1	⟨1	⟨1	3.82ns	9.85**
pH (o)	2	61.17**	79.82**	4.46*	31.37**
r×o	2	⟨1	⟨1	⟨1	⟨1
Error	15				
Total	23				

[+] Block was given to 4 kinds of soil in the present RCB analysis ; Redox treatment is oxidized and reduced condition ; pH treatment has 3 levels, pH 6, 7 and 8 ; r×o=interaction.

[++] Silica reactivity is a modification of ISR[11] ; C-type slope is the slope of linear regression of silica sorption isotherm ; Freundlich intercept is the intercept of Freundlich equation (Eq. 2) ; Tempkin slope is the slope of Tempkin equation (Eq. 3).

[+++] C-type slope and Tempkin slope was analyzed after transforming the data to logarithmic scale.

Table 5. The effects of pH and redox condition on silica sorption by the soil determined by using the "C-type slope" as a parameter.

pH LEVELS	C-TYPE SLOPE[+]			
	Oxidized condition	Reduced condition	Mean	Difference
6	13.0 c[++]	10.8 c	11.9 c	2.2ns
7	90.7 b	42.1 b	51.6 b	18.6ns
8	198.6 a	146.9 a	172.8 a	51.7ns
Mean	90.8	66.63	78.74	24.2ns

[+] C-type slope is the slope of linear regression to silica sorption isotherm.

[++] Numbers in a column followed by the same letter are not significantly different at the 5% level by DMRT.

ns = not significant.

time and temperature[1].

Tempkin equation enables to compare the rela-

Table 6. The effects of difference of soils on silica sorption determined by using "C-type slope" as a parameter.

KINDS OF SOILS	C-TYPE SLOPE[+]			
	Oxidized condition	Reduced condition	Mean	Difference
Luisiana	270.7 a[+]	122.1 a	196.4 a	148.6ns
Maahas	46.5 b	95.5 b	71.0 b	−49.0ns
Yongji	39.5 b	42.0 b	40.8 b	−2.5ns
Mangyeong	6.7 c	6.8 c	6.8 c	−0.1ns
Mean	90.8	66.6	78.7	24.2ns

[+] C-type slope is the slope of linear regression to silica sorption isotherm.

[++] Numbers in a column followed by the same letter are not significantly different at the 5% level by DMRT.

ns = not significant.

tive P adsorption capacity of various soils corresponding to empirically observed equilibrium p concentration that lead to optimum growth of crop[20,33]. The slope of the Tempkin equation can be a measure of the P buffering capacity[4].

The failure in the correct evaluation of treatment effects by the above two parameters seemed to be caused by a horizontal shift of the sorption isotherm curve to the right in reducced soils due to color interference and weighting of the lower values in the logarithmic scale included in both equations.

The "Silica reactivity" is a modification of ISR (Index of Silica Reactivity) Which has been proposed by Gallez et al.[11] as an empirical parameter to evaluate the surface properties of the soils. The ISR is defined as the percentage of soluble Si lost from the initial solution after 7 days equilibration at pH 9.2. The "Silica reactivity" in the present study is the percentage of lost silica after 4 hours equilibrium without fixing pH level. This parameter is purely an empirical description while the other three have more or less physical meaning.

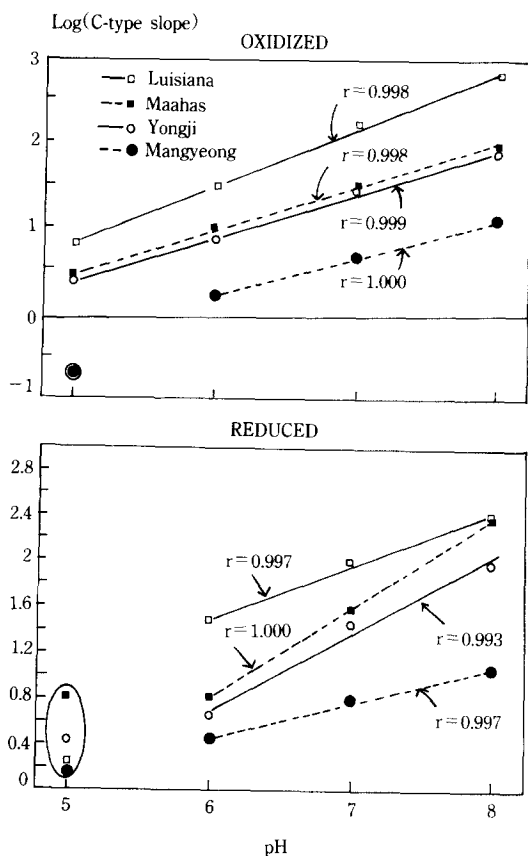The introduced "C-type slope" is a good para-

Fig 8. pH-dependent "C-type slope" of various soils incubated under oxidized or reduced condition. Data in circles are excluded in regressional analysis.

meter because the simple linear regression fits the sorption isoterm as good as the Freundlich and Tempkin equation (Table 3). Moreover, it is not affected by the result of color interference during measurement and by the sensitisity of logarithmic scale. Because the result of color interference adversely affects the intercept but not the slopes of the regression and the "C-type slope" is obtained in normal scale unlike the intercept of Freundlich equation and the slope of Tempkin equation.

The "C-type slope" increased exponentially with increase of pH, showing almost a linear regression in semi-logarithmic scale when some data points at low pH were excluded because of the possibi-

lities of wrong determination due to the color interference (Fig. 8). This characteristics implys that the "C-type slope" can be the useful tool for the asnalysis of sorption isotherms. Further studies are required to group the soils using the "C-type slope" for the more convenient use of the parameter.

Among the soil physico-chemical properties all forms of Fe and Al oxides and OM showed significant correlation with the "C-type slope" and the "Silica reactivity" at all pH levels. Among them Fe_d was most highly correlated to the "C-type slope", while OM was the case in the "Silica reactivity" (Table 7).

Multiple linear regression was conducted to find out the important factors influencing the Si sorption (Table 8). When the "C-type slope" was used as a parameter, Fe_d among soil physicochemical properties was the only important factor influencing Si sorption at all pH levels. However, when the "Silica reactivity" was used as a parameter, OM revealed the highest correlation with silica sorption (Table 8).

Correlation analysis reveals that the "C-type slope" is more superior than the "Silica reactivity" to discriminate factors on Si sorption. The "C-type slope" generally showed higher coefficients of determination than the "Silica reactivity" (Table 7). The influencing soil properties determined by multiple regression analysis using "C-type slope" did not change at different pH levels, whereas those determined by the "Silica reactivity" were not consistent. Moreover, the "Silica reactivity" emphasized too much the contribution of OM. According to the literatures Si sorption relies much on the effect of sesquioxies but not the direct effects of OM[3, 11, 24]. It has been reported that the oxidic surfaces of Al and Fe oxides are much more reactive than the silicate surface of clay minerals[3, 24].

Upon prolonged submergence dissolved Fe(II)

Table 7. Correlation coefficient between the "C-type slope" and "Silica reactivity" and soil physicochemical properties at three pH levels.

SOIL PROPERTIES	C-type slope			Silica reactivity		
	pH levels			pH levels		
	6	7	8	6	7	8
	Correlation coefficients(r)					
Fe_p (%)[+]	0.935**	0.900**	0.832*	0.932*	0.904**	0.828*
Fe_o (%)	0.901**	0.802*	0.737*	0.912**	0.885*	0.817*
Fe_d (%)	0.973**	0.948**	0.860**	0.920**	0.814**	0.712**
Al_p (%)	0.917**	0.874**	0.759*	0.891**	0.833**	0.758*
Al_o (%)	0.965**	0.898**	0.795**	0.914**	0.815**	0.722**
Al_d (%)	0.950**	0.921**	0.800*	0.855**	0.707**	0.598*
OM (%)	0.939**	0.875**	0.805*	0.961**	0.910**	0.834*
Clay (%)	0.651 ns	0.605 ns	0.655 ns	0.764 ns	0.809 ns	0.763 ns
CEC (meq/100g)	0.183 ns	0.159 ns	0.292 ns	0.355 ns	0.484 ns	0.491 ns
Eh (mV)	−0.062 ns	0.001 ns	0.003 ns	−0.020 ns	−0.218 ns	−0.206 ns

[+] Subscript p, o, and d denotes "pyrophosphate extractable", "acid oxalate extractable", and "dithionite-citrate extractable", respectively.

[++] * = significant at the 5% level ; ** = significant at the 1% level ; ns = not significant.

Table 8. Multiple linear regression of the "C-type slope" and the "Silica reactivity" at three pH levels to soil chemical properties using stepwise method with standardized variables.

Parameters	pH levels	Regression Equation	Coefficient of determination
C-type slope	6	$Y=0.973**Fe_d{}^+$	0.947**
	7	$Y=2.716**Fe_d-1.787*Al_o$	0.970**
	8	$Y=0.860**Fe_d$	0.739**
Silica reactivity	6	$Y=0.961**OM$	0.923**
	7	$Y=-2.070**Fe_d{}^{\cdot}+2.94* {}^*Fe_p$	0.969**
	8	$Y=0.834**OM$	0.696**

[+] Subscript d and o denotes "acid oxalate extractable" and "dithionite-citrate extractable", respectively.

precipitates to $Fe_3(OH)_8$[32], to $FeCO_3$[36], and to Fe(II)-Fe(III) hydroxycarbonates[45]. Such compounds have a large surface area and are responsible for increases in sorption capacities[46]. The surface area of oxide minerals increases with decrease of crystallinity[43]. Oxalate extractable iron (Fe_o) increased in reduced soil and slightly increased the zero point of net charge as well as pH_o in the current

srudy(Table 2, Figs. 3 and 4).

When samples of ferric and aluminum oxides of similar crystallinity are compared, the aluminum oxides are more effective in sorbing Si than the ferric oxides[18]. The scale of the Index of Silica Reactivity follows the order kaolinite<<goethite<gibbsite[11].

Referring to the above findings, higher correlation was expected for Si sorption to Al_o and Al_d than to Fe_o and Fe_d and to Fe_o rather than to Fe_d. However, Fe_d showed the highest correlation coefficient. The multiple regression analysis revealed that only Fe_d significantly affected silica sorption (Table 8) probably because Fe_d dominates the change of surface characteristics during the transformation of cryatalline iron oxide minerals to amorphous iron oxide minerals . Likely the impact of Al-oxides did not become evident because Al-oxides could not be properly determined and quantified as being stated earlier.

摘　　要

pH와 酸化還元 電位가 토양의 珪酸吸着에 미치는

영향을 보기위하여 두개의 필리핀토양과 두개의 한국 토양을 사용하여 室內에서 실험하였다. 규산의 等溫吸着은 等溫吸着의 分類體系에 의하면 弱한 L-type (漸近線的 增加)을 지닌 C-type(直線的 增加)에 屬하였다.

규산의 等溫吸着은 Freundlich와 Tempkin 等溫吸着式에 잘 맞았으나 Langmuir 等溫吸着式에는 잘 맞지 않았다. Molybdenum-blue 法에 의한 규산 發色時 還元 및 낮은 pH 條件에서 Fe^{2+} 이온에 起因된 것으로 보이는 發色障害가 나타났다.

Freundlich 式의 切片, Tempkin 式의 기울기, "Silica reactivity"와 "C-type slope"등 4개의 指標를 규산흡착에 미치는 處理效果 判定을 위한 指標로서 檢討하였다. 이들중 "Silica reactivity"와 "C-type slope"는 本 실험에서 提案된 指標였다. 4개의 指標 중 "C-type slope"가 가장 좋은 指標로 판명되었다. C-type 等溫吸着의 直線回歸는 Freundlich와 Tempkim式과 거의 同一한 높은 直線回歸 相關係數를 보였다. 또한 pH와 log(C-type slope)는 高度의 直線關係를 보였다.

C-type slope를 지표로 이용한 處理效果 分析결과 pH와 土壤種類는 규산의 토양흡착에 크게 영향을 미치는 반면 酸化還元 電位의 效果는 없었다.

모든 形態의 Al과 Fe 및 OM이 규산흡착과 高度의 相關을 보였으며 그 중 Fe_d가 寄與度가 가장 큰 成分으로 나타났다. 酸化알루미늄의 分別定量法이 確立되어 있지않은 結果 Al의 寄與度는 不確實하게 나타나는 것으로 보였다.

REFERENCES

1. BARROW, N. J. 1978. The description of phosphate adsorption curves. J. Soil Sci. 29 : 477~462.

2. BAO, XIE-MING. 1985. Iron and manganese. Pages 69~70 *in* physical Chemistry of Paddy Soils, T. R. Yu (Ed.). Springer-Verlag, Berlin/Science Press, Beijing.

3. BECKWITH, R. S. AND R. REEVE. 1963. Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. Aust. J. Soil Res. 1 : 157~168.

4. ────, ──── 1964. Studies on soluble silica in soils. II. The release of monosilicic acid from soils. Aust. J. Soil Res. 2 : 33~45.

5. BIGGAR, J. W. AND M. W. CHEUNG. 1973. Adsorption of picloram (4-amino-3, 5, 6- trichloropicolinic acid) on panoche, Ephrata, and palouse soils : a thermodynamic approach to the adsorption me-

chanism. Soil Sci. Soc. Am. Proc. 37 : 863~868.

6. BLACK, C. A. 1965. Methods of soil analysis. Part 2. Amer. Soc. Agron. Inc. Madison, Wisconsin, USA.

7. BORGGAARD, O. K. 1987. Moessbauer spectroscopy of ferric oxides and hydroxides. Mossbauer Eff. Ref. Data J. 2 : 76~94.

8. BOWMAN. B. T. 1982. Conversion of Freundlich adsorption K values to the male fraction format and the use of Sy values to express relative adsorption of pesticides. Soil Sci. Soc. Am. J. 46 : 740~743.

9. BROWN, T. H. AND R. L. MAHLER. 1987. Effects of phosphorus and acidity on the levels of Si in the soil solution extracted from a Palouse silt loam. Soil Sci. Soc. Am. J. 51 : 674~677.

10. CAMPBELL, A. S. AND U. SCHWERTMANN. 1985. Evaluation of selective dissolution extractants in soil chemistry and mineralogy by differential X-ray diffraction. Clay Miner. 20 : 515~519.

11. GALLEZ, A., A. J. HERBILLON, AND A. S. R. JUO. 1977. Characteristics of silica sorption and solubility as paramerers to evaluate the surface properties of tropical soils : I. The index of silica reactivity. Soil Sci. Soc. Am. J. 41 : 305~310.

12. GILES, C. H., D. SMITH, AND A. HUITSEN. 1974. A general treatment and classification of the solute adsorption isotherm. J. Colloid Interface Sci. 47 : 755~765.

13. GILLMAN. G. P. AND G. UEHARA. 1980. Charge characteristics of soils with variable and permanent charge minerals : II. Experimental. Soil Sci. Soc. Am. J. 44 : 252~255.

14. GOLDBERG, S. AND R. A. GLAUBIG. 1988. Boron and silicon adsorption on an aluminum oxide. Soil Sci. Soc. Am. J. 52 : 87~91.

15. GREENLAND, D. J., S. BURCHILL, AND H. B. HAYES. 1981. Adsorption. Pages 221~400 *in* The chemistry of Soil Proesses. D. J. Greenland and M. H. B. Hayes (ed.). John wiley and Sons, New York.

16. HAYWARD, D. O. AND B. M. W. TRAPNELL. 1964. Chemisorption, 2nd Ed. London : Butterworth and Co. Ltd.

17. HINGSTON, F. J. AND M. RAUPACH. 1967. The reaction between monosilicic acid and aluminum hydroxide. I. kinetics of adsorption of silicic acid by aluminum hydroxide. Aust. J. Soil Res. 5 : 295~309.

18. JONES, L. H. P. AND K. A. HANDRECK. 1963. Effect of iron and aluminum oxides on silica in solution in soils. Nature. 198 : 852~853.

19. ──────────────. 1967. Silica in soils, plants, and animals. Adv. Agron. 19 : 107~149.

20. KLAGES, M. G., R. A. OLSEN, AND V. A. HABY. 1988. Relationship of phosphorus isotherm to $NaHCO_3$-extractable phosphorous as affected by soil properties. Soil Sci. 146 : 85~91.

21. KUNDU, D. K. 1987. Chemical kinetics of aerobic soils and rice growth. ph. D. Thesis. Indian Agr. Res. Inst.

22. LEE, K. S. 1988. Silica. Pages 144~150 *in* Methods of soil chemical analysis (In Korean). K. H. Han (ed.). Sammi Press, Seoul.

23. LOVELAND, P. J. AND P. DIGBY. 1984. The extraction of Fe and Al by 0.1 N orthophosphate solutions : a comparison of some techniques. J. soil sci. 35 : 243~250.

24. MCKEAGUE, J.A. AND M. G. CLINE. 1963. Silica in soil solution

(II). The adsorption of monosilicic acid by soil and by other substances. Can. J. Soil Sci. 43 : 83~96.

25. ———— AND J. H. DAY. 1966. Dithionite and oxalate extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46 : 13~22.

26. NIAES. 1987. Interpretation of the mechanism for the reaction of silica fertilizers to the rice plant. (In Japanese). Annual Reprot of National Institute of Agro-Environmental Sciences : 75~80.

27. PARFITT, R.L. AND C. W. CHILDS. 1988. Estimation of forms of Fe and Al : A review and analysis of contrasting soils by dissolution and Moessbauer methods. Aust. J. Soil Res. 26 : 121~144.

28. PARK, C. S. 1971. Studies on the relation between available silica content and the effect of silicate, distribution pattern of available silica content and requirement in Korean paddy top soil. (In Korean, (Eng. Summary)). The Research Reports, Rural Development Adm., Korea 13(9).

29. PATRICK, W. J. JR. AND C. N. REDDY. 1978. Chemical changes in rice soils. Pages 361~379 in Soils and Rice. IRRI, Los Banos, Philippines.

30. ————, D.S. MIKKELSEN, AND B.R. WELLS. 1985. Plant nutrient behavior in flooded soil. In fertilizer technology and use (3rd ed.) Soil Sci. Soc. Am., Madison, WI.

31. POLYZOPOULOS, N. A., V. Z. KERAMIDAS, AND H. KIOSSE. 1985. phosphate sorption by some alfisols of Greece as described by commonly used isotherms. Soil Sci. Soc. Am. J. 49 : 81~84.

32. PONNAMPERUMA, F. N. 1972. The Chemistry of submerged soils. Adv. Agron. 24 : 29~96.

33. ROY, A. C. AND S. K. DE DATTA. 1985. Phosphate sorption isotherms for evaluating phosphorus requirement of wetland rice soils. Plant soil 86 : 185~186.

34. SANYAL, S. K. AND S. K. DE DATTA. 1991. Chemistry of phosphorus transformations in soil. In B. A. Stewart (Ed.). Advances in Soil Science, Vol. 16.

35. SCHOFIELD, R. K. 1949. The electric charges on clay particles. J. Soil Sci. 1 : 1~8.

36. SCHWAB, A. P. AND W. L. LINDSAY. 1983. Effect of redox on the solubility and availability of iron. Soil Sci. Soc. Am. J. 47 : 201~205.

37. SPOSITO, G. 1980. Derivation of the Freundlich equation for ion exchange reactions in soils. Soil Sci. Soc. Am. J. 44 : 652~654.

38. SUMIDA H. AND N. OHYAMA. 1988. Silica content in the supernatant obtained by the incubation under submerged conditions. Jpn, J. Soil Sci. Plant Nutr. 59 : 593~600.

39. TAKAHASHI, K. 1981. Relationship between the available silica contents in the soils and application effects of iron slag on the rice growth. Shigoku Agric. Res. Rep. 38 : 75~114.

40. ———— AND K. NONAKA. 1987. Available silica in submerged soils. II. Development and application of new silica analysis method for the diagnosis of silica fertility. Shigoku Agri. Res. Rep. 47 : 16~39.

41. TAYLOR, R. M. 1987. Non-silicate oxide and hydroxides. In A.C.D. Newman (Ed.) Chemistry of clay and clay minerals. John Wiley & Sons, New York.

42. VAN RAIJ, B. AND M. PEECH. 1972. Electrochemical properties of some Oxisols and Alfisols in the tropics. Soil Sci. Soc. Am. Proc. 36 : 587~593.

43. VEMPATI, R. K. AND R. H. LOEPPERT. 1988. Chemistry and mineralogy of Fe-containing oxides and layer silicates in relation to plant available iron. J. Plant Nutr. 11 : 1557~1574.

44. WEAVER, R. M., J. K. SYERS, AND M. L. JACKSON. 1968. Determination of silica in citrate-bicarbonate-dithionite extracts of soils. Soil Sci. Soc. Am. Proc. 32 : 497~501.

45. WILLETT, I. R. 1987. Phosphorus dynamics in relation to redox processes in flooded soils. Trans. 13th Congr. Int. Soil Sci. Soc. 6 : 748~755.

46. WILLETT, I. R. AND M. L. HIGGINS. 1978. Phosphate sorption by reduced and reoxidized rice soils. Aust. J. Soil Re. 16 : 319~326.

47. YOON, J. H. AND K. S. HWANG. 1984. The effect of additions of lime and starch on the silica sorption characteristics in submerged paddy soil. Korean Soc. Soil Sci. Fert. 17(1) : 35~38.