KINETICS OF DISSOLUTION OF NONCRYSTALLINE OXIDES AND CRYSTALLINE CLAY MINERALS IN A BASIC TIRON SOLUTION

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Abstract—The dissolution behavior of five noncrystalline oxides, montmorillonite, kaolinite, chlorite, and sepiolite in a basic tiron solution was studied at pH 10.5 and 80°C. The results show that for montmorillonite the concentrations of Al and Fe ions dissolved in the treating solution were diminished because of cation-exchange reactions of the sample in the suspension. To explain these observations, a mass-balance equation for the specified cation in solution was formulated, which consisted of both a dissolution term and an ion-exchange term. The several parameters of this differential equation were fitted to allow the calculated results to represent the experimental findings. Using these values, an equation lacking an ion-exchange term was also solved numerically. Thus, a dissolution curve was described, which would have been obtained had no cation exchange taken place. From these equations, the error resulted from the cation-exchange capacity of samples in chemical dissolution methods can be evaluated. According to this estimation, and assuming the value for a 1-hr treatment, an error of about 15% was determined for the amount of noncrystalline components contained in the specimen in this investigation.

要旨 － 塩基性タイロン溶液（ pH 10.5，80℃ ）中における5種類の非晶質酸化物とモンモリロナイト、カオリナイト、緑泥石およびセピオライトの溶解挙動について調べた。その結果、モンモリロナイトの場合、陽イオン交換反応のために、処理液中に溶出したAlおよびFeイオンの濃度は減少することが分かった。この観測結果を説明するため、液相中の着目陽イオンに関して、溶解とイオン交換の両方の項からなる質量収支式を導いた。この微分方程式中のいくつかのパラメータは、実験結果と計算結果が一致するように決定された。これらの値を用いて、上の質量収支式からイオン交換の項を除去した方程式を数値的に解くことにより、もし陽イオン交換反応がなかったら得られたであろう溶解曲線を求めた。これらの方程式により、化学溶解法において、試料の陽イオン交換能のために生ずる誤差を評価することができることを示した。この見積もりによれば、1 hr処理における溶液中の各イオン濃度から、非晶質物質の量を求めるとするならば、本報で示したような場合で、約15％の測定誤差が生ずる。

INTRODUCTION

Crystalline and noncrystalline phases in clays and sediments are difficult to separate physically from one another. Chemical dissolution methods have been widely applied to this problem, because they are relatively simple to carry out. These methods have used sodium hydroxide (Hashimoto and Jackson, 1960) and sodium carbonate (Follett *et al.,* 1965), pyrophosphate (Alexandrova, 1960), and oxalate (Schwertmann, 1964) as dissolution agents. A method using a basic tiron solution was proposed by Biermans and Baert (1977), who reported that the optimum condition for separating the noncrystalline from the crystalline soil fraction was obtained using 0.1 M tiron solution buffered at pH

10.5 and extracting at 80°C for 1 hr. Comparing this method with the other methods, Kodama and Jaakkimainen (1982) showed that the tiron method was more efficient in the selective dissolution of noncrystalline substances than the others.

The tiron method has been used in the authors' laboratory to characterize noncrystalline components in some soils; however, an unexpected behavior was observed for cation-exchangeable soils in the dissolution of the specified oxides, that is, the amount of Al and Fe dissolved appeared to reach a maximum and then to decrease with time in the tiron solutions.

In the present investigation, the dissolution behavior of several crystalline and noncrystalline substances was

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Table 1. Specimens used in dissolution experiments.

Material	Specific surface area (m²/g)	Cation-exchange capacity (meq/100 g)	Sample preparation	Reference
Noncrystalline				
Silica A	4.7	—	<2-μm fraction of ground silica glass.	—
Silica B	621	—	ground synthetic silica gel.	—
Alumina A	351	—	dried synthetic alumina sol, ground and heated at 550°C for 24 hr.	—
Volcanic ash A	114	54.5	<2-μm fraction, from the Aso Volcano, Kakino, Kumamoto, Japan.	Henmi *et al.* (1981)
Volcanic ash B	475	34.0	<2-μm fraction, from Kanto loam at Imaichi, Japan.	Henmi *et al.* (1983)
Crystalline				
Montmorillonite	34	99.6	<2-μm fraction, Na⁺-saturated "Kunipia G", supplied by Kunimine Industrial Company, Yamagata, Japan.	Hayashi (1963)
Kaolinite	10.5	6.0	<2-μm fraction, "Kaolinite" supplied by Kampaku Industrial Company, Tochigi, Japan.	Oinuma and Hayashi (1968)
Chlorite	37.1	8.4	<2-μm fraction, from Wanibuchi mine, Shimane, Japan.	Sakamoto and Sudo (1958)
Sepiolite	114	4.6	<2-μm fraction, from Kuzuu mine, Tochigi, Japan.	Imai *et al.* (1969)

studied in a basic tiron solution. To explain these dissolution behaviors, a mass-balance equation of the specified cation in liquid phases has been proposed. This equation, which consists of both a dissolution term and an ion-exchange term, can describe the unexpected behavior of the concentration change and correct the measurement error caused by the cation-exchange capacity of samples.

EXPERIMENTAL

Materials

The specimens used in the dissolution experiments are listed in Table 1, together with their specific surface area measured by the BET method, their cation-exchange capacities, and the preparation method of the samples. Volcanic ashes and synthetic materials were used as noncrystalline substances to carry out the experiments over a wide range of specific surface area. To examine the difference of the dissolution rate of between crystalline and noncrystalline materials, four clay minerals were used. The details on the clay minerals and the volcanic ashes were described in each reference in Table 1. Montmorillonite was washed in a Na$_2$CO$_3$ solution; hence, the interlayer cation was exchanged to Na⁺. Although very pure crystalline clay minerals were used, trace quantities of noncrystalline substances may have been present as impurities. X-ray powder diffraction patterns of all samples were made and are shown in Figure 1.

Tiron solution

A tiron solution was prepared as reported by Kodama and Hayashi (1985). Initially, 0.1 mole of tiron (C$_6$H$_4$Na$_2$O$_8$S$_2$) was dissolved in 800 ml of distilled water, 100 ml of a 0.5 M Na$_2$CO$_3$ solution was added, and the solution was mixed by agitation. Finally, the pH was adjusted to 10.5 by 4 M NaOH solution, and the total volume was adjusted to 1 liter with distilled water. The dissolution experiments were also performed using a 0.05 M Na$_2$CO$_3$ solution at pH 10.5, to compare them with the results obtained using the tiron solution.

Procedure

The tiron treatment basically followed that reported by Kodama and Hayashi (1985). The substances in Table 1 were dried at 105°C for 24 hr, 25 mg of the dried specimen was weighed into a polypropylene Erlenmeyer flask, and after 30 ml of the basic tiron solution or Na$_2$CO$_3$ solution had been added, the total weight of the flask was measured. The top of the flask was loosely wrapped with aluminum foil, and the flask was shaken in a water bath controlled at 80°C for various periods of time. As soon as the shaking was completed, the flask was rapidly cooled to room temperature using an ice-water bath. The flask was weighed after it had been wiped, and the difference in weight between before and after shaking was assigned to the loss of water due to evaporation. Residual solids in the solution were separated by centrifugation at 5000 rpm for 10 min. The supernatant was preserved for chemical analyses.

Analysis

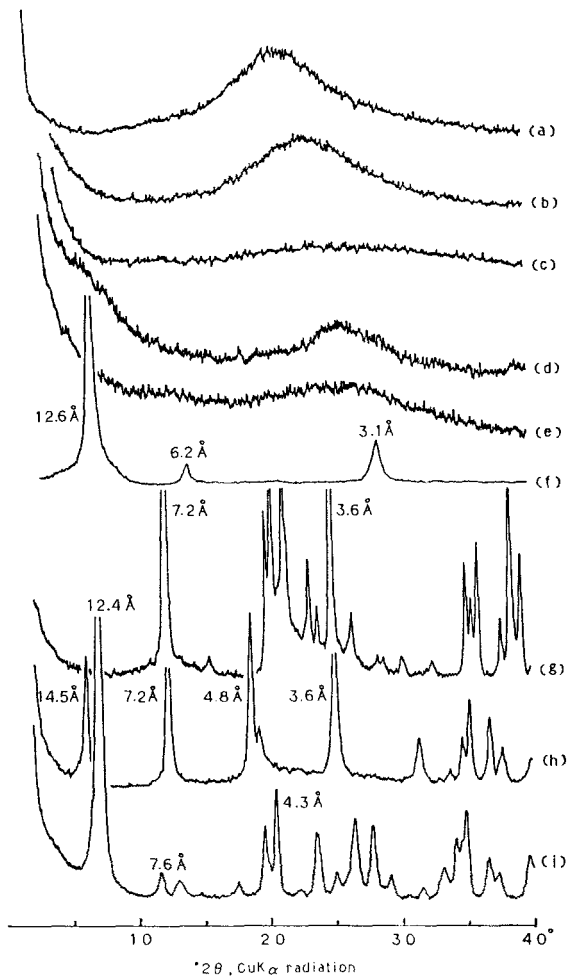X-ray powder diffraction (XRD) patterns were obtained with a Rigaku Denki X-ray diffractometer using

Figure 1. X-ray powder diffraction patterns of (a) silica A, (b) silica B, (c) alumina A, (d) volcanic ash A, (e) volcanic ash B, (f) montmorillonite, (g) kaolinite, (h) chlorite, (i) sepiolite.

Figure 2. Dissolution behavior of silica A in tiron solution at 80°C, pH 10.5.

Ni-filtered CuKα radiation and a scanning speed of 2'2θ/min. The cation-exchange capacity (CEC) was measured at pH 7 by the procedure of Wada and Harada (1969), using Ca^{2+} for saturation.

Al and Fe ions were analyzed quantitatively by atomic absorption spectroscopy. Because the absorption of Fe was enhanced by the coexistence of tiron in the solution, the data were corrected using standard solutions. Because the absorption of Al was enhanced by the coexistence of Si, this interference was also corrected using standard solutions. The coexistence of Fe had almost no influence on the absorption of Al under the condition of the analysis. Spectrophotometric determination of Si was performed using ammonium molybdate, because the sensitivity of this element was very low in atomic absorption spectroscopy. In the spectrophotometr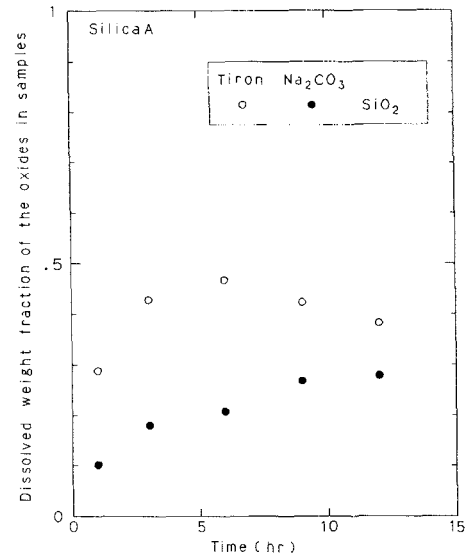ic determination, the absorption of Si was virtually free from interference of Fe, Al, and tiron under the given condition.

RESULT AND DISCUSSION

Dissolution behavior of the noncrystalline substances

The dissolution behavior of silica A is shown in Figure 2. In this and in Figures 3–5, measured concentrations of the specified ions were converted to those in the oxide forms. These values were then divided by the total amount (25 mg) of the sample used for extraction and expressed as weight fractions. The amount of dissolved species produced by the tiron treatment was greater than that produced by the sodium carbonate treatment. For the tiron treatment, the Si ion concentration in the solution began to decrease at about 6 hr. A similar decrease was found for silica B, which consisted of silica gel. In addition, many floccules were observed in the solution that had been treated for 6 hr. These results suggest that the flocculation involving silica started at about 6 hr in the solution. Therefore, treatments of more than a few hours duration should be avoided for a precise quantification for silica-containing specimens.

Figure 3 shows the dissolution behavior of volcanic ash A and illustrates that the tiron solution dissolved noncrystalline substances more efficiently than the sodium carbonate solution. The dissolution was completed in about 1 hr. Volcanic ash B and alumina A reacted similarly, suggesting an optimum condition of the treatment to be 80°C for 1 hr and pH 10.5, which Biermans and Baert (1977) have shown.

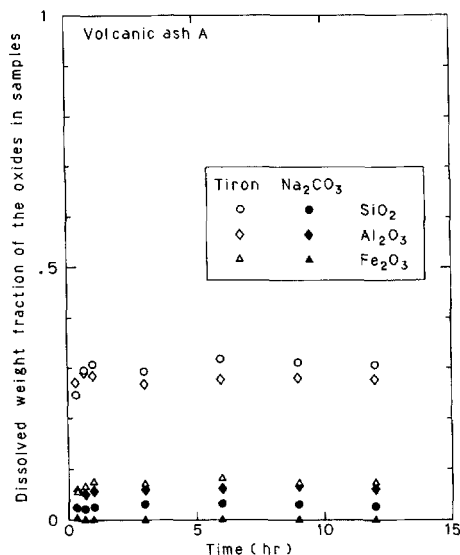Figure 3. Dissolution behavior of volcanic ash A in tiron solution at 80°C, pH 10.5.

Figure 4. Relation between log specific surface area of the used materials and weight fraction of the sum of SiO₂ and Al₂O₃ dissolved within 1 hr in the sample.

Effect of specific surface area on dissolution

Figure 4 shows the relation between the fraction dissolved and the specific surface area of the used materials. These plots fall into two groups: (1) noncrystalline substances and (2) crystalline minerals. For noncrystalline substances, the greater the specific surface area of a specimen, the greater was the dissolution. Therefore, the surface area of the substances will be considered when the kinetics of dissolution is discussed in a later section.

Dissolution behavior of clay minerals

The dissolution of chlorite, kaolinite, and sepiolite was completed in about 1 hr; however, the amounts of these specimens that dissolved were much less than those of the noncrystalline substances. Possibly, some of the material that dissolved was from noncrystalline impurities in the samples rather than from the crystalline minerals themselves. If they had been from the crystalline minerals themselves, each ion concentration would have increased gradually with time during the prolonged time treatment.

On the other hand, the dissolution behavior of montmorillonite was quite different from those of the other minerals (Figure 5). The amounts of Al and Fe ions in the solution rapidly increased, showed a maximum after about 1 hr, and, then, decreased. A gradual increase after the decrease was probably caused by dissolution of crystalline phases. The amount of Si in solution, however, gradually increased during the dissolution period, probably due to dissolution of crystalline phases. Because montmorillonite has a high cation-exchange capacity, Al and Fe ions in solution may
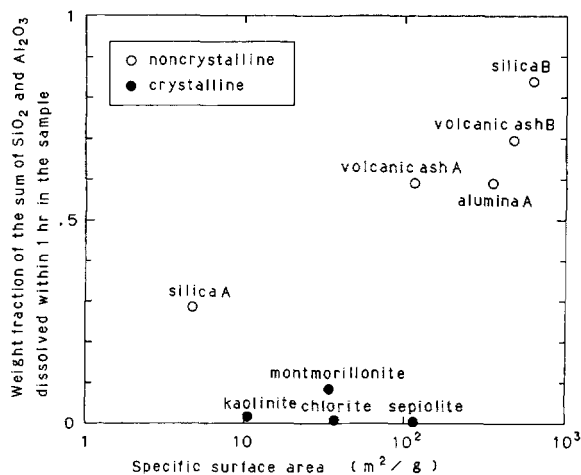
have been entered the interlayers of the mineral by cation-exchange.

To examine this possibility, the difference in expansion produced by the kinds of interlayer cations was measured before and after the treatments: the XRD patterns of the oriented montmorillonite were obtained for untreated, tiron-treated (1 hr), and sodium carbonate-treated (1 hr) specimens, which had been wetted by distilled water. No 001 peak was found in the XRD pattern of the wetted, oriented specimen of untreated montmorillonite, because of large swelling by water caused by the presence of Na as the chief interlayer cation. The d(001) value was 18.8 Å for the wetted specimens of the tiron- and sodium carbonate-treated montmorillonite samples. Na ions were probably exchanged by Al and/or Fe ions during the treatment. Inasmuch as the montmorillonite used in this experiment had a CEC of 99.6 meq/100 g, exchangeable Al ions constituted about 1.7 wt. % Al₂O₃, roughly corresponding to the difference between the maximum Al in solution after 40 min and the minimum after 3 hr during the tiron treatment. The cation-exchange reaction by montmorillonite in the tiron solution appears to have been responsible for the concentration of each cation in the solution not being equal to the amount actually dissolved. Consequently, the amount actually dissolved must be estimated using kinetics based on the factors of both dissolution and ion-exchange.

Analysis of the dissolution behavior of montmorillonite

As shown in Figure 5, the dissolution behavior of montmorillonite was different from that of the other substances, because cation content of the solution was reduced by the cation-exchange reaction. As a result,

the measurement of ions from the noncrystalline substances by this method does not give accurate values.

The following analysis was therefore made to quantify the actual dissolution of materials containing minerals having significant cation-exchange capacities. Assumptions for the analysis were as follows: (1) The montmorillonite flakes were randomly aggregated in solutions, and, thus, the aggregates were spherical particles of radius R. (2) Intraparticle diffusion was expressed by solid phase diffusion. (3) The rate of cation-exchange reaction far exceeded that of diffusion. (4) Mass transfer resistance at the particle surface was negligible. (5) The specimen consisted of montmorillonite plus a small amount of noncrystalline oxides, and the weight of the specimen (W) and the volume of the solution (V) were constant during the treatment.

Intraparticle diffusion may be represented as follows:

$$\frac{\partial q}{\partial t} = Ds\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial q}{\partial r}\right), \qquad (1)$$

where Ds = coefficient of intraparticle diffusion (m^2/s), q = particle phase concentration of the specified cation (mole/kg), r = radial coordinate (m), and t = time (s) (Bird *et al.*, 1961). Mass balance in solutions can be expressed for a specified cation as:

$$V\frac{dC}{dt} = kS(t)(Ci - C) - \frac{3WDs}{R}\cdot\frac{\partial q}{\partial r}\bigg|_{r=R}, \qquad (2)$$

where C = liquid phase concentration of the specified cation (mole/m^3), Ci = saturated concentration (mole/m^3), k = rate constant of dissolution (m/s), and $S(t)$ = surface area contacting with solutions (m^2). The first term on the right hand side of the equals sign is the dissolution rate of the specified cation from the specimen. The rate constant k contains factors other than the surface area and concentration difference. The second term is the reduction rate for the cation from the liquid phase.

The initial (I.C.) and boundary conditions (B.C.) are as follows:

I.C.: at $t = 0$, $q = 0$ and $C = 0$ for $0 \leqq r \leqq R$, (3)

B.C.$_1$: at $t > 0$, $\frac{\partial q}{\partial r} = 0$ for $r = 0$, (4)

B.C.$_2$: at $t \rightarrow \infty$, $q = q_i$ for $0 \leqq r \leqq R$, (5)
and
B.C.$_3$: at $t > 0$, $q = q_i$ for $r = R$. (6)

Eq. (6) corresponds to assumption (3). The value of q on particle surfaces is equal to zero at $t = 0$; q quickly reaches q_i, which is a saturated value, after the start of the experiment. Therefore, in calculation, discontinuity between Eq. (3) and Eq. (6) was treated as follows: q reached q_i during the first step of numerical integration in Eq. (2).
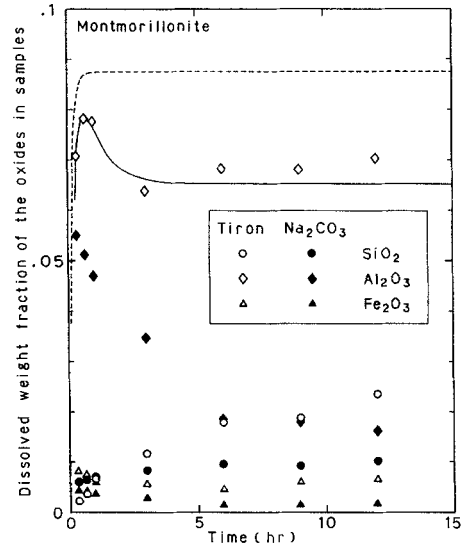

Figure 5. Dissolution behavior of montmorillonite. Solid line was calculated from Eq. (2) in text using the experimental results of Al_2O_3 in tiron solution. Dashed line is the result calculated without cation-exchange term in Eq. (2), using the experimental results of Al_2O_3 in tiron solution. Parameter values for the calculation: $a = 4.0 \times 10^4$; $b = 1.45$; $kSi = 1.5 \times 10^{-4}$ m^3; $Ds/R^2 = 4.0 \times 10^{-5}$ /s; and $Ci = 0.719$ mole/m^3.

The calculation requires first that Eq. (1) be solved and that mass flux of the specified cation through particle surfaces be calculated. This result is then substituted in the second term of Eq. (2), in which adequate values are substituted for a, b, kSi, Ds/R^2, and Ci, such that the calculated values closely fit the experimental results well (see Appendix for details involving parameters a, b, and kSi). Next, the second term is eliminated from Eq. (2), and the same values of the parameters obtained above are substituted. The calculation without the cation-exchange reaction is then performed.

Figure 5 also gives the calculated result which fit the experimental results of Al_2O_3 for the tiron solution. The solid line corresponds to the experimental results. The dashed line is identical to that which would have been obtained had no cation-exchange taken place. If the value of the 1-hr treatment is adopted as the amount of noncrystalline components contained in the specimen (in accordance with the Biermans and Baert's criteria), the error is about 15%.

SUMMARY

The dissolution behavior of several crystalline and noncrystalline substances in a basic tiron solution at pH 10.5, 80°C was examined. For specimens containing montmorillonite, which has a high cation-exchange capacity, the concentrations of Al and Fe ions released from noncrystalline substances in the tiron solution

untreated

18.8 Å

tiron-treated

Na$_2$CO$_3$-treated

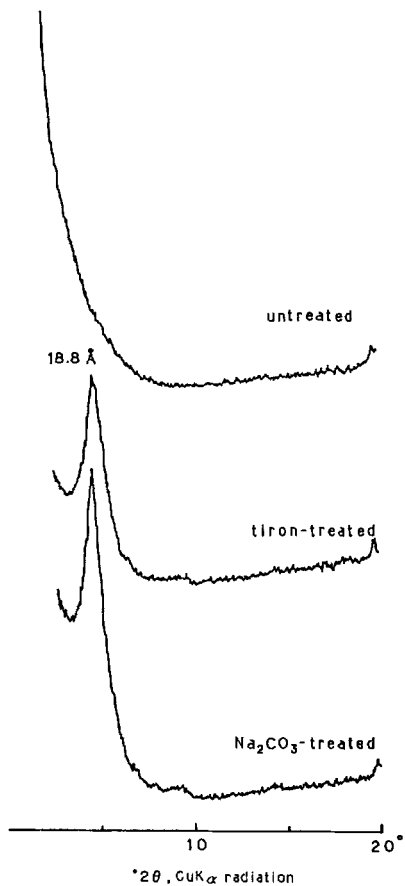10   20°

°2θ, CuKα radiation

Figure 6.   X-ray powder diffraction patterns of the oriented slide preparation of untreated, tiron-treated, and sodium carbonate-treated montmorillonites, wetted by distilled water. Time for each treatment = 1 hr.

Figure 7.   Schematic diagram of assumed S(t), surface area in contact with treatment solutions.

APPENDIX

Description of S(t)

S(t) in the first term of Eq. (2) is not specific surface area measured by the BET method, but surface area in contact with treatment solutions as a function of time. Such surface areas cannot be measured; hence, a following function was assumed in this study. Figure 7 shows a schematic diagram of assumed S(t). Here, a new function defined by the following equation is introduced:

$$P(t) = \int_0^t S(t)dt \bigg/ \int_0^\infty S(t)dt . \qquad (7)$$

P(t) is a kind of probability function and can be approximated by means of a Weibul distribution function in consideration of the shape shown in Figure 7 as:

$$P(t) = 1 - \exp\left(-\frac{t^b}{a}\right). \qquad (8)$$

Thus,

$$S(t) = \frac{b}{a} Si\ t^{b-1} \exp\left(-\frac{t^b}{a}\right), \qquad (9)$$

where

$$Si = \int_0^\infty S(t)dt . \qquad (10)$$

increased initially and then decreased with time. The XRD patterns of the oriented slide preparations wetted by H$_2$O indicated that the interlayer cation of the specimen treated in the tiron solution was exchanged by Al and/or Fe ions. To clarify this unexpected observation, a mass-balance equation was developed for the specified cation in solutions on the basis of dissolution and ion-exchange. This equation approximately explained the experimental results. Furthermore, based on this equation, the effect of the ion-exchange on dissolution behavior was evaluated.

Dissolution in these systems, however, is still more complicated than described above, and problems involving such reactions as ion-exchange and flocculation still exist in chemical dissolution methods.

ACKNOWLEDGMENTS

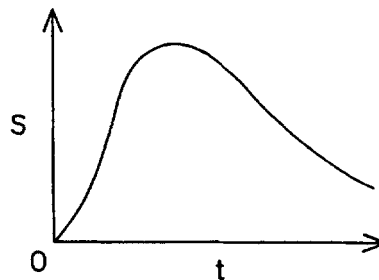The authors express their appreciation to A. Shimoyama of Tsukuba University for helpful criticism.

REFERENCES

Alexandrova, L. N. (1960) The use of sodium pyrophosphate for isolating free humic substances and their organomineral compounds from soil: *Soviet Soil Sci.,* 190–197.
Biermans, V. and Baert, L. (1977) Selective extraction of amorphous Al, Fe and Si oxides using an alkaline tiron solution: *Clay Miner.* **12**, 127–135.
Bird, R. B., Stewart, W. E., and Lightfoot, E. N. (1961) *Transport Phenomena:* Wiley, New York, 357–360.
Follett, E. A. C., McHardy, W. J., Mitchel, B. D., and Smith, B. F. L. (1965) Chemical dissolution techniques in the study of soil clays: Part 1: *Clay Miner.* **6**, 23–34.
Hashimoto, I. and Jackson, M. L. (1960) Rapid dissolution

of allophane and kaolinite-halloysite after dehydration: in *Clays and Clay Minerals, Proc. 7th Natl. Conf., Washington, D.C., 1958,* Ada Swineford, ed., Pergamon Press, New York, 102–113.

Hayashi, H. (1963) Montmorillonite from some bentonite deposits in Yamagata Prefecture, Japan: *Clay Sci.* **1,** 50–56.

Henmi, T., Nakai, M., Seki, T., and Yoshinaga, N. (1983) Structural changes of allophanes during dry grinding: Dependence on SiO_2/Al_2O_3 ratio: *Clay Miner.* **18,** 101–107.

Henmi, T., Tange, K., Minagawa, T., and Yoshinaga, N. (1981) Effect of SiO_2/Al_2O_3 ratio on the thermal reactions of allophane. II. Infrared and X-ray powder diffraction data: *Clays & Clay Minerals.* **29,** 124–128.

Imai, N., Otsuka, R., Kashide, H., and Hayashi, H. (1969) Dehydration of palygorskite and sepiolite from the Kuzuu district, Tochigi Pref., central Japan: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1,* L. Heller, ed., Israel Universities Press, Jerusalem, 99–108.

Kodama, H. and Hayashi, H. (1985) Comparative study on chemical dissolution techniques—Application to identification and quantitative determination of non-crystalline silicates: *Nendo Kagaku* **25,** 139–147 (in Japanese).

Kodama, H. and Jaakkimainen, M. (1982) A comparative study of selective chemical dissolution methods for separating non-crystalline components produced by grinding of silicates: in *Proc. Int. Clay Conf., Bologna, Pavia, 1981,* H. van Olphen and F. Veniale, eds., Elsevier, Amsterdam, 399–410.

Oinuma, K. and Hayashi, H. (1968) Infrared spectra of clay minerals: *J. Toyo University, General Education (Nat. Sci.) No. 9,* 57–98.

Sakamoto, T. and Sudo, T. (1958) Magnesium-rich chlorite from the Wanibuchi mine, Shimane Prefecture, *Miner. Journ.* **1,** 348–358.

Schwertmann, U. (1964) The differentiation of iron oxides in soil by extraction with ammonium oxalate solution: *Z. Pflanzenernaehr. Dueng. Bodenkd.* **105,** 194–202.

Wada, K. and Harada, Y. (1969) Effect of salt concentration and cation species on the measured cation-exchange capacity of soils and clays: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1,* L. Heller, ed., Israel Universities Press, Jerusalem, 561–571.