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Author(s)	Ishiguro, Munehide; Nakaishi, Katsuya; Nakajima, Tomo
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Saturated hydraulic conductivity of a volcanic ash soil affected by repulsive potential energy in a multivalent anionic system

Munehide Ishiguro* , Katsuya Nakaishi, and Tomo Nakajima

M. Ishiguro, Faculty of Environmental Science and Technology, Okayama Univ., 3-1-1 Tsushima-naka, Okayama 700-8530, Japan; K. Nakaishi, Faculty of Agriculture, Ibaraki Univ., Ami, Inashiki-gun, Ibaraki 300-0393, Japan; and T. Nakajima, Raito Kogyo Co.Ltd., Kudan-Kita, Chiyoda-Ku, Tokyo 102-8236, Japan. *Corresponding author (ishi@cc.okayama-u.ac.jp)

ABSTRACT

Although repulsive potential energy among soil clay particles generates swelling and dispersion, and thereby changes in soil hydraulic conductivity, the relationship between hydraulic conductivity and repulsive potential energy has not been evaluated. In this paper, saturated hydraulic conductivity (K) changes of allophanic Andisol (volcanic ash soil), which is characterized by a number of pH-dependent charges, during dilute acid leaching and their relation with repulsive potential energy were examined. When nitric acid at pH 3 or 4 was leached, K decreased rapidly. On the other hand, the decrease in K became smaller as the ratio of sulfate in the dilute acid increased. From the results of zeta potential measurement and calculation of repulsive potential energy between the clay particles, we concluded that the decrease in K for an acid solution of high nitrate ratio was due to swelling and dispersion of the soil induced by electrostatic repulsive potential energy. Because sulfate was adsorbed on the clay surface, the repulsive potential energy decreased as the ratio of sulfate in the dilute acid increased. Then, the surface adsorption maintained the flocculation of the soil and inhibited the decrease in K.

２００３ Hydraulic conductivity is an important physical parameter of soil. It is well-known that dispersion and deposition of clays in the narrow necks of conducting pores reduce saturated hydraulic conductivity (K). The swelling of clay may also narrow water-conducting pores in soil (Quirk and Schofield, 1955; McNeal and Coleman, 1966; Shainberg and Singer, 1990).

Swelling and clay dispersion occur due to an increase of electric repulsive force among soil particles. The repulsive force increases with increase of the absolute value of the surface potential of the clay, or with decrease of ion concentrations or valency of the counterion (Iwata, 1995). Therefore, the charge characteristics of soil and valency of the counterion are very important when K is considered.

Recently, acid rain has become a serious problem throughout the world. The adverse effects of acid rain on the hydraulic conductivity of soils should be assessed. Because the charge of soils affects their K and soils have pH-dependent charges, pH is an important factor for K. Suarez et al. (1984) found K at pH 9 to be less than at pH 6 for a montmorillonitic and a kaolinitic soil. They suggested that differences in pH effects on K among soils were probably due to differences in quantities of variable charge minerals and organic matter. Chiang et al. (1987) showed that Cecil soil (clayey, kaolinitic, thermic Typic Kanhapludult) was easily dispersed and K was sensitive to small changes in electrolyte concentration, sodium adsorption ratio (SAR), or pH. They also suggested that Davidson (clayey, kaolinitic thermic Rhodic Kandiudult) and Iredel (fine, montmorillonitic, thermic Typic Hapludulf) soils were flocculated and insensitive to changes in electrolyte concentration and pH except at very high SAR.

Allophanic Andisol contains a substantial pH-dependent charge, and its K is therefore strongly affected by pH. Nakagawa and Ishiguro (1994) found that K for allophanic Andisol decreased during leaching with HCl solution at pH 3 and NaOH solution at pH 11. Kakubo et al. (1995) and Matsukawa et al. (1998) noted that the soil K decreased during HNO_3

leaching and remained constant during H_2SO_4 leaching. These studies suggest that acid rain affects *K*. Ishiguro and Nakajima (2000) experimentally elucidated the relationships among *K*, pH and clay dispersion in the soil profile during dilute HNO_3 and H_2SO_4 leaching. Although electrical repulsive potential energy among soil clays generates dispersion and swelling of the soil, which in turn induce a decrease in *K*, the relationship between the repulsive potential energy and the change in *K* has not been studied.

The objective of this study was to determine the mechanism of the change in *K* of allophanic Andisol soil during dilute acid leaching. For this purpose, zeta potentials of the soil clay were measured and the repulsive potential energies were evaluated. Dispersion characteristics of the soil were also measured. Because the main contaminants of acid rain are HNO_3 and H_2SO_4, dilute solutions of these contaminants were used in the experiment.

MATERIALS AND METHODS

Allophanic Andisol (Hapludand) was obtained from a field at the National Institute of Agro-Environmental Sciences in Tsukuba, from the 4Bw1 horizon. Its physical and chemical properties are listed elsewhere (Ishiguro and Nakajima, 2000).

Hydraulic Conductivity Studies

In order to clarify the effects of mixtures of dilute HNO_3 and H_2SO_4, K was determined at a constant hydraulic gradient of 5 m m^{-1}. To control the constant hydraulic gradient, a mariotte bottle and a tube connected to the bottom of the soil column through a small water-filled head space and filter net were used. The mariotte bottle was used to maintain a constant water pressure on the top of the soil column. The pressure at the bottom of the soil column was maintained at almost zero by placing the outlet of the tube at the same height as the bottom surface of the soil. Influent solutions were mixtures of HNO_3 and H_2SO_4 at pH 3 or pH 4. Mixed ratios of NO_3 concentration (mol_c m^{-3}) to NO_3+SO_4 concentration (mol_c m^{-3}) in the solutions (NO_3 ratio) were 0, 50, 70, 90 and 100 %. The solutions at pH 3 and pH 4 were equivalent to electrolyte concentrations of 1.0 and 0.1 mol_c m^{-3}, respectively. The experimental procedure was as follows:

1. A column (3.2 cm in diam. by 3 cm in height) was packed with <2-mm sieved field-moist soil to a bulk density of 510 kg m^{-3} (same as under field conditions).
2. The soil column was saturated by capillary rise with 1000 mol_c m^{-3} solution containing a mixture of $NaNO_3$ and Na_2SO_4 for one day.
3. 100 cm^3 (an approximately 5 pore volume) of the solution was percolated through the column to saturate the clay charges with the solutes. Then, a 1 mol_c m^{-3} solution containing a mixture of $NaNO_3$ and Na_2SO_4 was percolated through the column until the concentrations of the outflow and inflow solutions were identical. The NO_3 ratio of the solution was the same as that of the 1000 mol_c m^{-3} solution used for the saturation.

4. Finally, a solution containing a mixture of HNO_3 and H_2SO_4 with the same NO_3 ratio at pH 3 or pH 4 was percolated through the column. The flow rate was measured during acid leaching and K was calculated following Darcy's law. Each solution was changed quickly using 2 mariotte bottles and a three-way stopcock.

Dispersion Studies

Light transmittance of soil suspensions was measured to examine the relation between K and dispersion. NO_3 ratios in the suspended solutions were also 0, 50, 70, 90 and 100 %. The procedure was as follows:

1. <2-mm sieved, field-moist soil (0.02 g by dry soil) was equilibrated with a 1000 $mol_c\ m^{-3}$ solution containing a mixture of $NaNO_3$ and Na_2SO_4.
2. The soil was equilibrated with ($NaNO_3$ + HNO_3 + Na_2SO_4 + H_2SO_4) solution at an electrolyte concentration of 0.1 $mol_c\ m^{-3}$ and a specified pH from 4 to 5.4, or at an electrolyte concentration of 1 $mol_c\ m^{-3}$ and a specified pH from 3 to 5.2. The NO_3 ratio of the equilibrated solution was the same as that of the 1000 $mol_c\ m^{-3}$ solution in procedure 1.
3. 30 cm^3 of the soil/solution mixture was shaken for 1 min in a 50 cm^3 tube. After 18 h of settling, 15 cm^3 were sampled from the upper portion (2.5 cm in depth) of the mixture, and light transmittance was measured using visible light. Transmittance intensities were 0 % through a shaded plate and 100 % through pure water in a cell.

Measurement of Zeta Potential

In order to evaluate the electrostatic repulsive potential energy in the soil, the zeta potentials of the soil clay in the suspensions were measured. The zeta potentials were derived using electrophoretic light scattering (ELS-800; Otsuka electronics, Japan). NO_3 ratios in the suspended solutions were also 0, 50, 70, 90 and 100 %. The procedure was as follows:

1. <2-mm sieved, field-moist soil (0.02 g by dry soil) was equilibrated with a 1000 $mol_c\ m^{-3}$ solution containing a mixture of $NaNO_3$ and Na_2SO_4.
2. The soil was equilibrated with a ($NaNO_3$ + HNO_3 + Na_2SO_4 + H_2SO_4) solution at an electrolyte concentration of 0.1 $mol_c\ m^{-3}$ and a pH of about 4, or at an electrolyte concentration of 1 $mol_c\ m^{-3}$ and a pH of about 3. The NO_3 ratio of the equilibrated solution was the same as that of the 1000 $mol_c\ m^{-3}$ solution in procedure 1.
3. 30 cm^3 of the soil/solution mixture was shaken for 1 min in a 50 cm^3 tube. When the suspension was dispersed, 15 cm^3 were sampled from the upper portion (2.5 cm in depth) of the mixture after 1 h of settling. When flocculated, 15 cm^3 were sampled after 30 min of settling.
4. The sample suspension was agitated with sonication, diluted 10 times with pure water, and agitated with sonication for an additional 5 minutes. Then, the zeta potential was measured.

Electrical Repulsive Potential Energy

Electrical repulsive potential energies between the soil clay particles were estimated in order to clarify the mechanism of the decrease in *K*.

These energies were derived from the measured zeta potentials.

In the case of low potentials, a potential at the distance x from the charged clay surface, Ψ, can be approximated as follows:

$$\Psi = \Psi_s \exp(-\kappa x), \quad [1]$$

where Ψ_s is the potential of the clay surface. κ is defined as follows:

$$\kappa^2 = \frac{F^2 \Sigma z_i^2 C_{o,i}}{\varepsilon RT}, \quad [2]$$

where F is the Faraday const., z_i is the valence of ion i, $C_{o,i}$ is the concentration of ion i in the bulk solution (mol m^{-3}), ε is the permitivity of the liquid, R is the gas constant, and T is the absolute temperature. If a zeta potential, ζ, is used instead of Ψ_s in Eq.[1], we can get the potential distribution from the plane of the zeta potential to the bulk solution.

We consider that two clay particles approach each other. Then, the potential at the midpoint between the clays, Ψ_m, is,

$$\Psi_m = 2\Psi, \quad [3]$$

where Ψ is the potential at the point when the clay exists alone. The concentration of ion i at the midpoint, C_i, is given as

$$C_i(x) = C_{0,i} \exp\left(-\frac{z_i F \Psi_m}{RT}\right). \quad [4]$$

The electrical repulsive force between the clays is the osmotic pressure at the midpoint. The osmotic pressure, Π, is,

$$\Pi = RT \Sigma (C_i - C_{o,i}). \quad [5]$$

Only concentrations of the counterions (NO_3, SO_4) were considered in calculation, because the influence of coions was negligible in Eq.[5].

We derive the repulsive potential energy, V_ζ, when the two clay

particles approach the plane of the zeta potential as follows:

$$V_\varsigma = -2\int_b^0 \Pi dD \quad , \qquad [6]$$

where D is the distance from the plane of the zeta potential to the midpoint, and b is the distance from the zeta potential plane to the boundary of the bulk solution. The point at which the repulsive potential energy is equal to 0 is given in the bulk solution.

RESULTS

Data for changes in relative *K* when leaching with dilute acid are given in Figs. 1 and 2. The abscissa shows the percolated amount of the dilute acid solution (m) as the height of solution when collected into a cylinder with the same sectional area as the soil column. The relative *K* is defined as the ratio of *K* during dilute acid leaching to *K* during percolation of a solution containing a mixture of $NaNO_3$ and Na_2SO_4 at 1 mol_c m^{-3} just before dilute acid leaching. Initial *K*s ranged from 6.9×10^{-6} to 1.1×10^{-4} m s^{-1}. The changes in *K*s differed with the NO_3 ratio in the inflow solution. *K*s decreased more rapidly as the NO_3 ratio increased, as shown in Figs. 1 and 2. For pH 3 solutions, *K* of 70 % NO_3 ratio initially decreased, but finally recovered to the initial value. *K* of 50 % NO_3 ratio maintained its initial value. On the other hand, *K* of 0 % NO_3 ratio increased slightly after 2.5 m percolation. For pH 4 solutions, *K* of 70 % NO_3 ratio showed a tendency similar to that of *K* of 90 % NO_3 ratio; i.e., both gradually

decreased. *K*s of 50 % ratio and 0 % NO_3 ratio slightly increased. The decrease in *K* at pH 3 for higher NO_3 ratio was much steeper than those at pH 4.

After the leaching experiments, the soil was removed from the column to examine the soil structure. Aggregates at the top of the column (= several mm thickness) had collapsed and larger pores had disappeared for the soils whose *K* decreased. No significant soil structural change could be visually detected for the soils whose *K* did not decrease. These results were similar to those in the former study for HNO_3 and H_2SO_4solutions (Ishiguro and Nakajima, 2000).

Light transmittances in soil suspensions are shown in Fig. 3. The transmittance decreased as the NO_3 ratio increased. NO_3 maintained a stable dispersion condition. The influence of pH on the suspensions at 1 $mol_c\ m^{-3}$ was not clear. The transmittance for the 0.1 $mol_c\ m^{-3}$ solution decreased as pH decreased. The transmittance for the 0.1 $mol_c\ m^{-3}$ solution was relatively lower than that for the 1 $mol_c\ m^{-3}$ solution.

The zeta potentials are given in Fig. 4. These potentials increased with increasing NO_3 ratio. There was a particularly steep increase near the 100% NO_3 ratio. The zeta potentials at pH 3 were larger than those at pH 4.

The calculated repulsive potential energies are shown in Fig. 5. These energies also increased as the NO_3 ratio increased. And again, the increase near the 100% NO_3 ratio was particularly steep. The potential energy became smallest at the 0 % NO_3 ratio. The repulsive potential energies at pH 3 were much larger than those at pH 4.

DISCUSSION

Based on the change in *K*, soil structure observations, dispersion studies, and repulsive potential energy calculations, it was clearly shown that *K* decreased by leaching with higher NO_3 ratio acid solution mainly as a result of swelling and dispersion of soil particles. Charge of allophanic Andisol is pH-dependent and thus positive charge predominates at low pH (Iimura, 1966; Okamura & Wada, 1983; Ishiguro et al., 1992) . At low pH, when the NO_3 ratio of the solution is higher, the positive charge generates electric repulsive potential energies among soil particles, as shown in Fig. 5. Then, swelling and dispersion (Fig. 3) occur. Larger water-conducting pores will consequently narrow.

On the other hand, when a lower NO_3 ratio solution was leached, the repulsive potential energy was much smaller (Fig. 5) and the soil particles remained in a flocculated condition (Fig. 3). Therefore, the *K* decrease was restricted (Figs. 1 and 2). Ishiguro et al. (submitted) showed that most of the adsorbed SO_4 was on the clay surface and that the degree of NO_3 adsorption was greatly reduced by the presence of SO_4 in the solution. That is, the diffuse double layer became thinner as SO_4 was adsorbed on the clay surface. Because the repulsive potential energy is generated when diffuse double layers overlap, the repulsive potential energy is reduced due to SO_4 adsorption on the clay surface. A large amount of SO_4 adsorption on the clay surface keeps the soil under flocculated condition. Therefore, at lower NO_3 ratio, *K* did not decrease, but rather increased slightly.

The repulsive potential energies at pH 3 and higher NO_3 ratio were higher than those at pH 4, as shown in Fig. 5. Because the soil swelled and was well dispersed under these higher repulsive potential energies, the *K*s at pH 3 and 90 % and 100 % NO_3 ratio decreased more rapidly than those at pH 4. Although the repulsive potential energy at pH 3 and 70 % NO_3 ratio was larger than those at pH 4 and 70 % and at pH 4 and 90 % NO_3 ratio, the *K* at pH 3 and 70 % NO_3 ratio recovered to the initial value and the *K*s at pH 4 and 70 % and 90 % NO_3 ratio decreased gradually. The calculated repulsive potential energy could not explain these *K* differences. One reason for this inconsistency may be the difference between the soil-column conditions in the *K* experiment and the dilute-suspension conditions for the measurement of the zeta potential. Moreover, as pointed out by Dukhin (1993), there is room for improvement in the method of measuring zeta potential. Nonetheless, these calculated results clearly showed that the decrease in *K* at higher NO_3 ratio was due to the higher repulsive potential energy among the soil particles.

The change in *K* was strongly influenced by the predominant clay minerals in the soil, allophane and imogolite. The point of zero net charge (PZNC) of allophane was pH 5.9, while that of imogolite was pH 7.2. Allophane and imogolite dispersed under PZNC (Karube et al., 1998: Karube, 1998). The results of dispersion studies at higher NO_3 ratio coincided with these findings.

The results of dispersion studies showed a clear tendency toward dispersion at higher NO_3 ratio and flocculation at lower NO_3 ratio. These results were in good agreement with those for the change in *K*. However,

though the transmittances at pH 4, higher NO_3 ratio and 0.1 $mol_c\ m^{-3}$ were lower than those at pH 3 and 1 $mol_c\ m^{-3}$, —i.e., the soil suspensions at pH 4 were more dispersed than those at pH 3 in the dispersion experiment—the decrease in K at pH 4 was more gradual than that at pH 3. These dispersion studies thus provided a rough estimation of the decrease in K, although they did not predict it precisely.

The transmittance for the 0.1 $mol_c\ m^{-3}$ solution decreased as pH decreased. This was probably due to the increase in the net charge with the decrease in pH. This tendency was very clear for the transmittance at 50 % NO_3 ratio. On the other hand, the K leached with the solution at 50 % NO_3 ratio and pH 4 did not decrease, but rather increased slightly, even though a large volume of dilute acid was applied. This inconsistency was thought to be related to the difference in measurement conditions. The soil suspension was shaken well in the dispersion study, while the soil was well packed in the column for the hydraulic conductivity study. The weaker repulsive force may have dispersed the soil clay in the dispersion study.

CONCLUSIONS

We calculated the repulsive potential energy of soil clay by means of its measured zeta potential under solutions having different ratios of NO_3 to SO_4. The results indicated that increasing repulsive potential energy induced swelling and dispersion, which in turn resulted in a decrease in K during the leaching of dilute acid with high NO_3 ratio. The counterion,

NO_3, is monovalent and resulted in a stronger electrostatic repulsive potential energy between soil particles than did SO_4. On the other hand, flocculation resulted in a slight increase in K during the leaching of dilute acid with high SO_4 ratio. The counterion, SO_4, is divalent and, moreover, has strong affinity for soils with pH-dependent charge. Most SO_4 ions were adsorbed on the clay surface and about 27 % of the adsorbed SO_4 were thought to have been chemically adsorbed at pH 3.3 (Ishiguro et al. 200?). Therefore, the attractive potential energy is probably stronger than the electrostatic repulsive potential energy between soil particles at higher SO_4 ratio.

In this study, attractive potential energy was not evaluated. Because the measured zeta potentials were thought to be valuable only for relative evaluation, the derived repulsive potential energies were also assumed to be valuable only for relative evaluation. Therefore, even if the exact attractive potential energy had been derived, absolute comparison with the calculated repulsive potential energy would not have been possible. Therefore, in order to more precisely evaluate repulsive potential energy for comparison with attractive potential energy, another exact method must be developed.

Because acid rain commonly contains both NO_3 and SO_4, the results obtained here provide information on the influence of acid rain on the permeability of allophonic Andisol. Not only acid rain, but also application of ammonium sulfate to crop fields sometimes decrease their soil pH. NO_3 and SO_4 coexist in such fields. Based on the present results, the ratio between these two anions has a direct effect on soil structure and

permeability.

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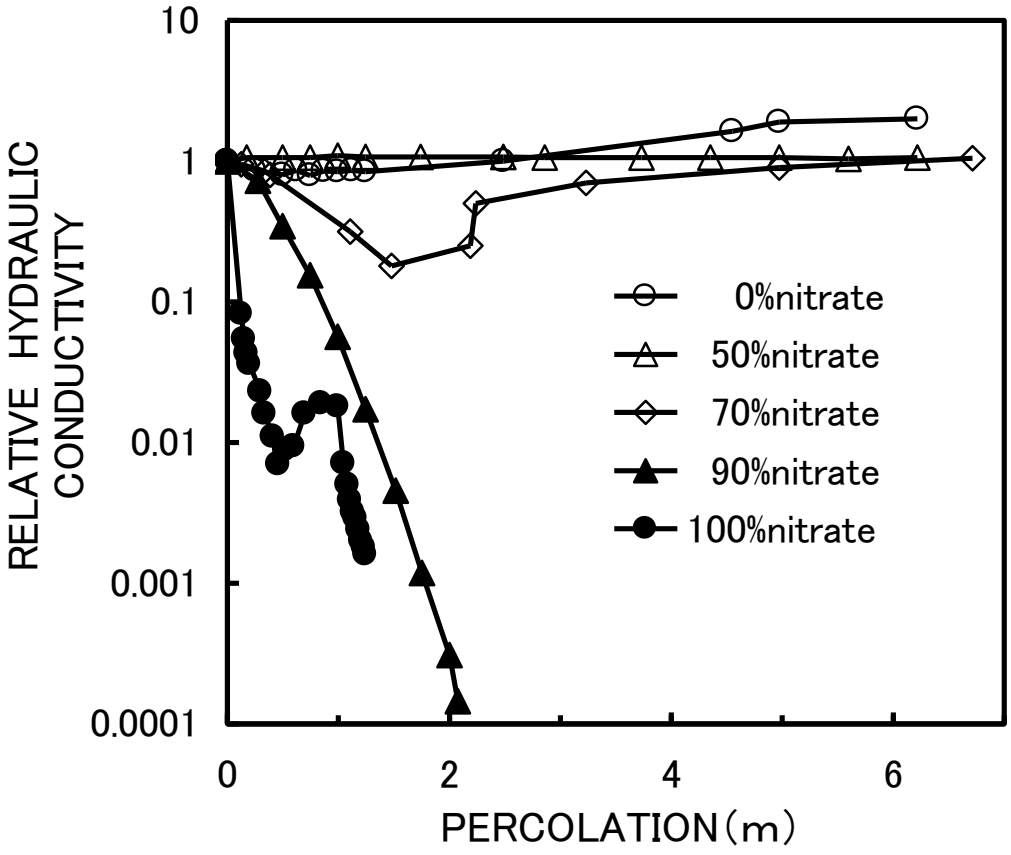


Fig. 1　Relative hydraulic conductivity change during the leaching of dilute acid at pH 3. The percentages denote the ratio of NO_3 to NO_3+SO_4 concentrations in the leaching acids.

(60% reduction)

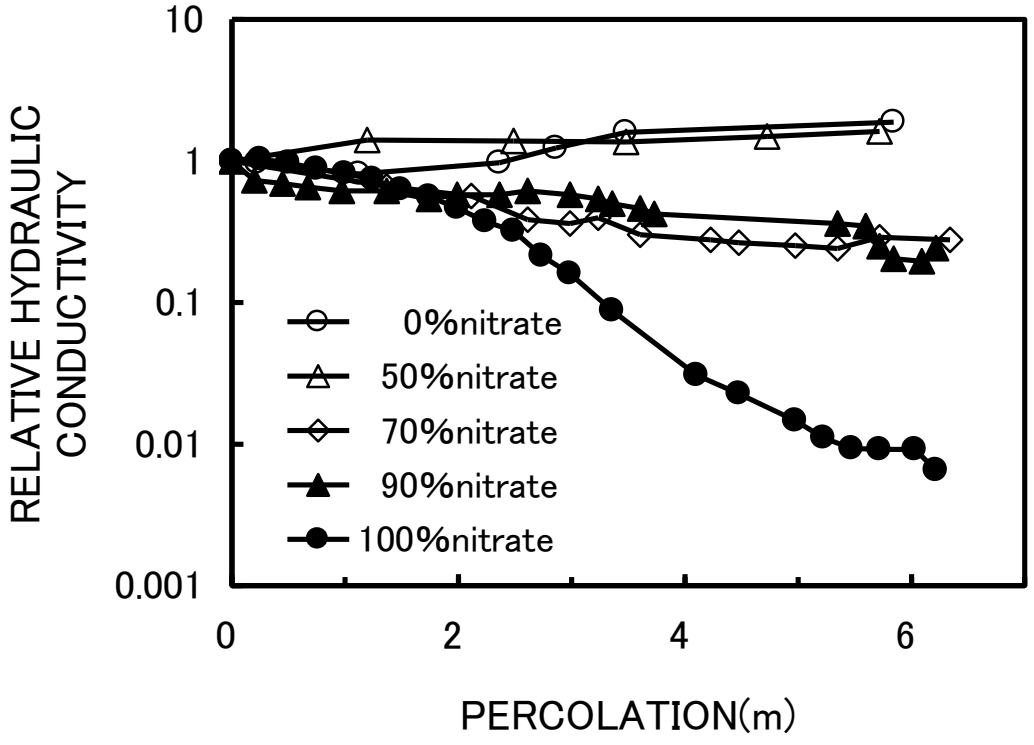
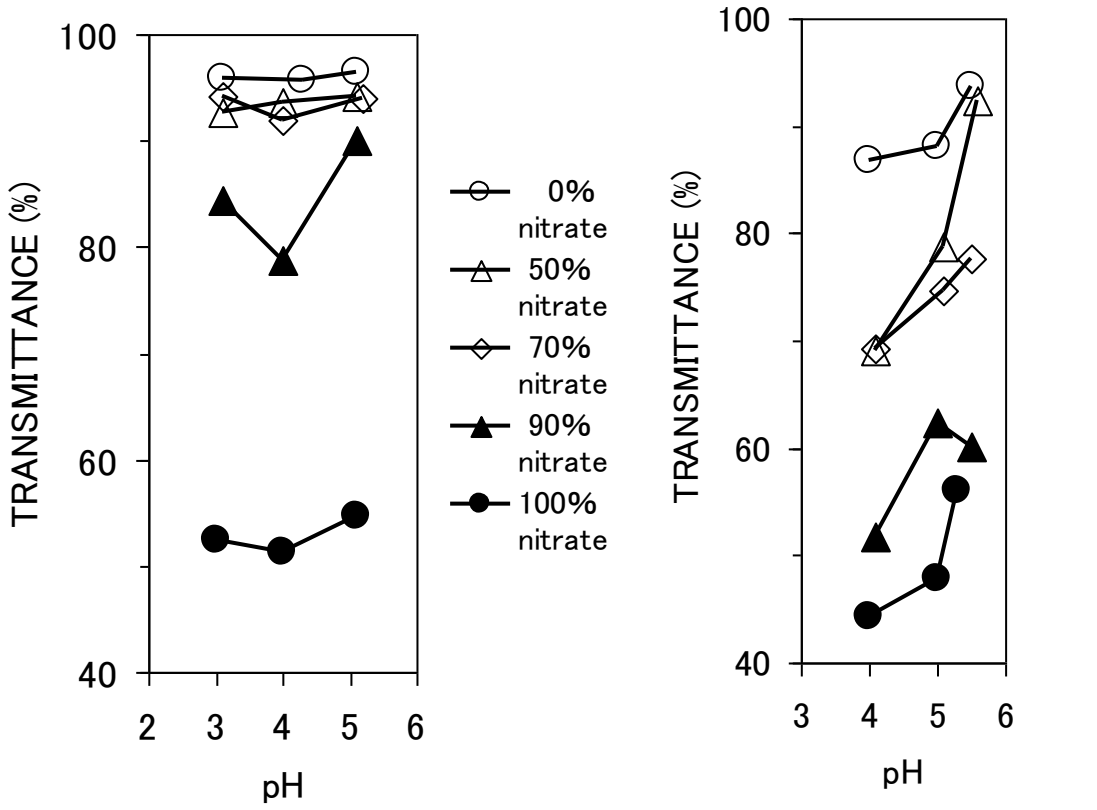


Fig. 2 Relative hydraulic conductivity change during the leaching of dilute acid at pH 4. The percentages denote the ratio of NO_3 to NO_3+SO_4 concentrations in the leaching acids.

(60% reduction)



a. Total conc. 1 $mol_c\ m^{-3}$ b. Total conc. 0.1 $mol_c\ m^{-3}$

Fig. 3 Light transmittance of the soil suspensions. The percentages denote the ratio of NO_3 to NO_3+SO_4 concentrations in the suspended solutions.

(60% reduction)

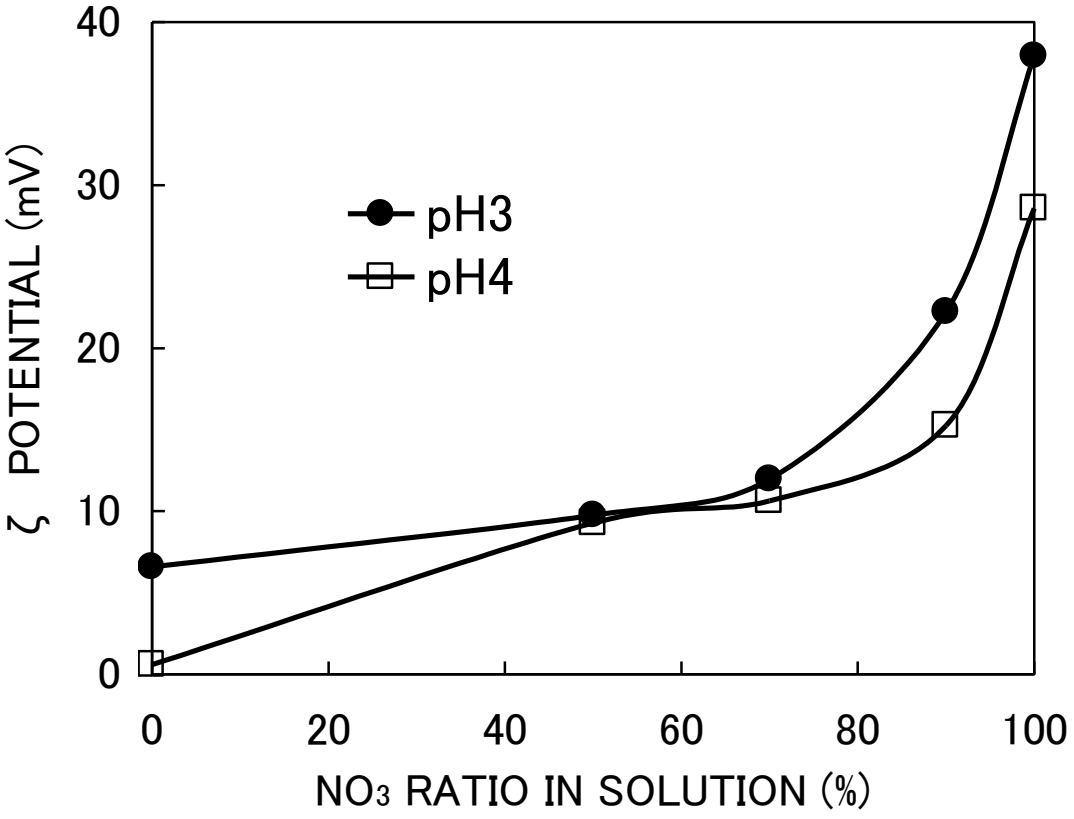


Fig. 4 Zeta potentials of the soil clay in dilute acids.

(60% reduction)

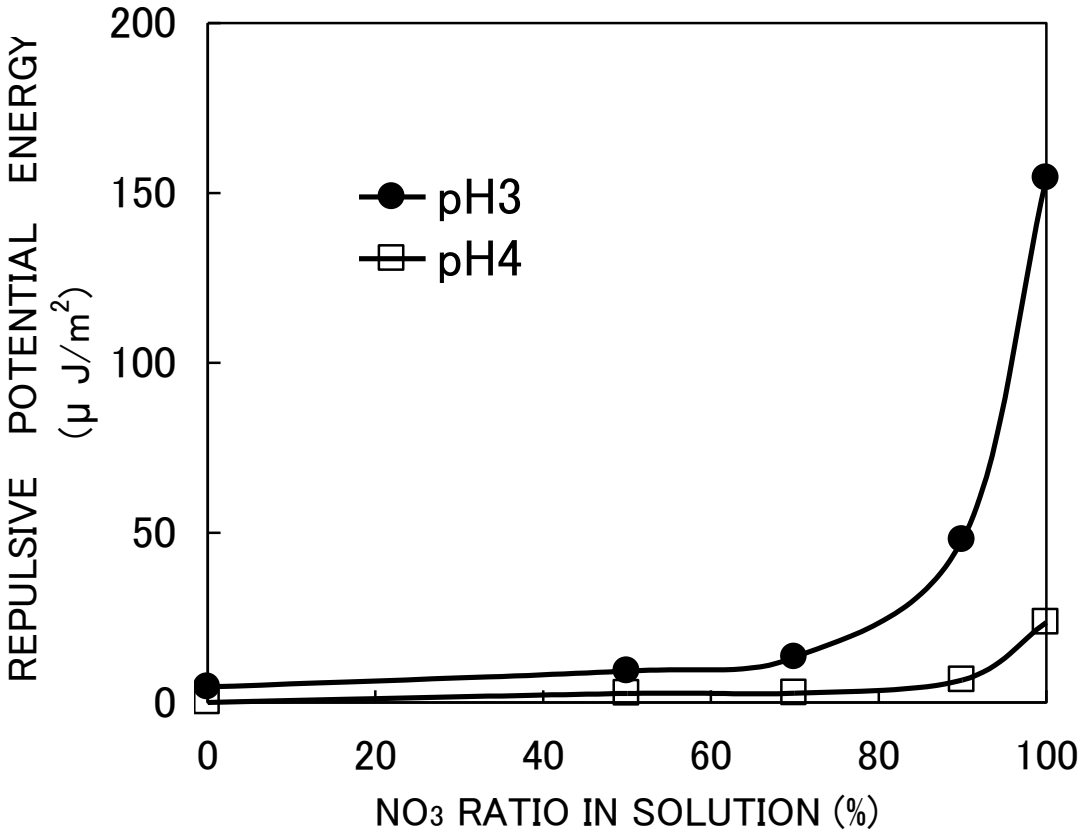


Fig. 5 Calculated repulsive potential energies in dilute acids.

(60% reduction)