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Ion Transport and Permeability in an Allophanic Andisol at Low pH

ABSTRACT

Allophanic Andisols have a significant pH-dependent charge. The positive charge increases and the negative charge decreases as pH decreases; therefore, anion movement becomes slower and cation movement becomes faster as pH decreases in the soil. At low pH, soil dispersion occurs easily due to electric repulsive force. The permeability of the soil then decreases because of structural changes that occur when dilute HCl or HNO_3 is percolated in the soil. However, soil permeability does not decrease when dilute H_2SO_4 is percolated in the soil. This is because SO_4^{2-} strongly adsorbs on the soil surface at low pH and the soil remains flocculated.

Keywords: ion transport, permeability, allophanic Andisol, soil dispersion, flocculation.

INTRODUCTION

Charge characteristics of soils are important because they strongly influence ion transport and soil structures. Commonly, soils possess pH dependent charges. Then, their effects are supposed to be significant with pH change. However, few studies on the effects of solution pH on miscible displacement experiment for exchanging ions have been reported (Chan et al. 1978; Chan et al. 1980a,b; Nielsen et al. 1986; Ishiguro et al. 1992). Studies on permeability change influenced by pH have been also few (Suarez et al. 1984; Chiang et al. 1987; Nakagawa and Ishiguro 1994,: Ishiguro et al. 2001). Allophanic Andisols, typical volcanic ash soils, have much amount of pH dependent charge (Iimura 1966; Okamura and Wada 1983). In this paper, ion transport, soil structure change and permeability change of the allophanic Andisol under low pH conditions were investigated and integrated the former researches.

MATERIALS AND METHODS

Soil. An allophanic Andisol (Hapludand) was obtained from a field at the National Institute

of Agro-Environmental Sciences in Tsukuba, Japan, from a depth of approximately 90 cm (4Bw1 horizon). The predominant clay minerals were allophane and imogolite. The sand content was 130 g kg^{-1}, silt content was 375 g kg^{-1}, and clay content was 495 g kg^{-1}. The organic C content was 11.6 g kg^{-1}. The <2-mm sieved field moist soil was used in all experiments. As pH decreased, the cation exchange capacity (CEC), the negative charge of the soil, decreased, and the anion exchange capacity (AEC), the positive charge of the soil, increased. Both the CEC and the AEC increased with an increase in ion strength.

Miscible displacement experiment. Sr^{2+} and Br^- breakthrough curves were obtained from saturated soil column tests. An acrylic column 30-cm long and 6.5-cm inside diameter (ID) was used. The hydraulic gradient was maintained at 0.5 m m^{-1}. A $SrBr_2$ solution at 0.01 mol_c L^{-1} at prescribed pH (pH 5.05, pH 5.75 or pH 7.2) was percolated into soil columns with the same pH condition (pH 5.05, pH 5.75 or pH 7.2) that had been initially saturated with a $CaCl_2$ solution at 0.01 mol_c L^{-1} at prescribed pH (pH 5.05, pH 5.75 or pH 7.2). Influent pH and effluent pH were same during this experiment. Sr^{2+} was analyzed by atomic absorption spectroscopy. Br^- was measured by ion chromatography.

Hydraulic conductivity study under different pH conditions. Saturated hydraulic conductivity (*K*) was determined at a constant hydraulic gradient of 3 m m^{-1} using a stainless steel column 3-cm long and 3-cm ID. The initial soil solution pH was under natural condition at about pH 6. The electrolyte concentration of the influent solutions (Na-H-Cl-OH system) was 1 $mmol_c$ l^{-1} under different pH conditions (pH 3 to 11).

Hydraulic conductivity study at pH 3. Values of *K* were determined at constant hydraulic gradient of 5 m m^{-1} using an acrylic column 3-cm long and 3.2-cm ID. The initial soil solution pH was under natural condition at about pH 6. The influent solutions were mixtures of HNO_3 and H_2SO_4 at pH 3 with different mixed proportions. The *K* distribution in the soil column was evaluated to measure the soil water pressure distribution using tensiometers. The pH distribution in the soil column was also measured.

RESULTS AND DISCUSSION

Fig.1

Miscible displacement experiment

The cation Sr^{2+} was found to move faster at lower pH levels because of the decrease in cation adsorption (Fig. 1a), and anion Br^- flowed out slower at lower pH levels due to the increase in anion adsorption (Fig. 1b). We were able to carry out accurate evaluation of ion movement in the soil using the adsorption amount (Ishiguro et al. 1992) and the one-dimensional convective-dispersive equation for ion exchange reaction (Ishiguro 1992).

Fig.2

Hydraulic conductivity study under different pH conditions

The results of the hydraulic conductivity study with different pH solution percolation are shown in Fig. 2. The values of *K* decreased drastically when HCl at pH 3 was percolated as shown in Fig. 2. *K* also decreased when NaOH at pH 11 was percolated, but this decrease was not as significant as the HCl at pH 3 (Nakagawa and Ishiguro 1994).

Photo 1, 2, 3

Photo 1 shows the surface structure of the soil before HCl percolation when soil aggregates were observed. Photo 2 shows the surface structure with collapsed aggregates after HCl at pH 3 percolation. Photo 3 is a vertical cross-section of a soil sample after 1.33 m^3 m^{-2} percolation of HCl at pH 3. In this case, soil aggregates in approximately the upper 7 mm had collapsed and larger pores were clogged, but the aggregates below this level maintained their structure. The collapse of the structure was caused by swelling of the soil aggregates and the clogging of large pores resulted from soil dispersion. This structural change in the upper layer caused a decrease in permeability.

Fig.3

The influence of the solution pH on soil dispersion is shown in Fig. 3 in which the vertical line indicates the dispersion ratio of the absorbance of the soil suspension after 12 hours of settling to that just after shaking. The soil was well dispersed in solutions with lower pH levels due to the predominant positive charge and in those with higher pH levels due to the predominant negative charge (Nakagawa and Ishiguro 1994). This phenomenon corresponds to the decrease in the saturated hydraulic conductivity.

Figs.4, 5

Hydraulic conductivity study at pH 3

Values of *K* were found to decrease when dilute HNO_3 was percolated in the soil as shown in Fig. 4. However, this decrease was restricted as the proportion of SO_4^{2-} to total anions in the solution increased. *K* distributions when 1.24 m^3 m^{-2} HNO_3 and H_2SO_4 solution was percolated

91 are shown in Fig. 5. Note that the value of *K* for HNO_3 decreased, particularly in the upper part of
92 the sample. This distribution corresponds to the structural change in the upper layer of the soil
93 shown in Photo 3. The *K* of the lower part of the soil was also found to decrease, probably due to
94 the clogging of the larger pores with soil particles from the upper layer. The *K* for H_2SO_4 almost
95 maintained its initial value with the exception that it increased somewhat in the upper part of the
96 soil. The pH became lower with decreasing the soil depth due to the acid percolation for both
97 conditions.

98 We also performed a dispersion study under the same solution conditions as those in the soil
99 column for the hydraulic conductivity study. The soil was well dispersed at higher proportions of
100 NO_3^- to the total anions in the solution, and well flocculated at higher proportions of SO_4^{2-},
101 corresponding to the change in *K* values; *K* is known to decrease when soil is well dispersed
102 (Ishiguro and Nakajima 2000, Ishiguro et al. 2003).

Fig.6

103 The electric repulsive potential energy between soil clay particles in mixtures of HNO_3 and
104 H_2SO_4 at pH 3 was calculated using the Gouy-Chapman theory (Ishiguro et al. 2003) and
105 electrophoretic mobility data as shown in Fig. 6. The horizontal axis in Fig. 6 indicates the
106 concentrations of NO_3^- and SO_4^{2-} ($mmol_c\ L^{-1}$) in the acid solution at pH 3. The repulsive potential
107 energy increased with an increase in NO_3^- proportion, and the increase near a NO_3^- concentration
108 of 1 $mmol_c\ l^{-1}$ was particularly steep. Repulsive potential energy caused dispersion and swelling
109 of the soil at higher NO_3^- proportions under low pH conditions, and permeability decreased as a
110 result of this dispersion and swelling. On the other hand, the repulsive potential energy decreased
111 and the soil became more flocculative with an increase in SO_4^{2-} proportion, because SO_4^{2-} forms
112 complexes on the clay surface at low pH (Ishiguro et al. 2003).
113

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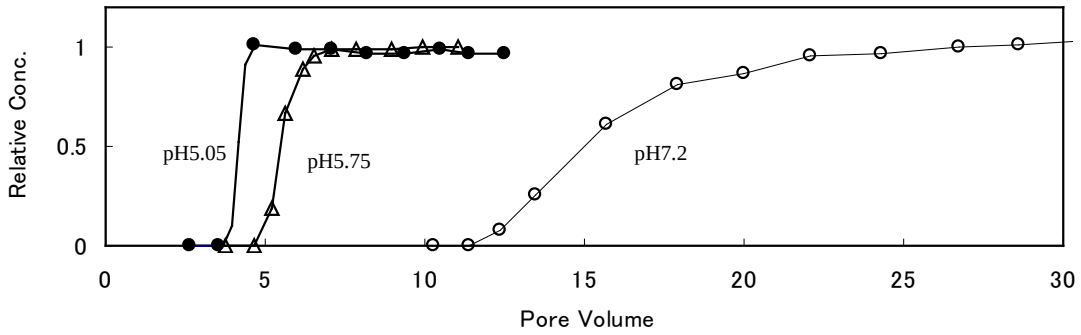
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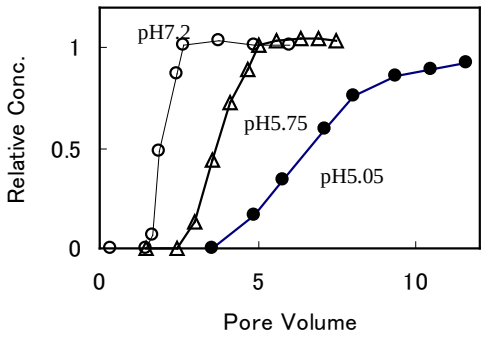
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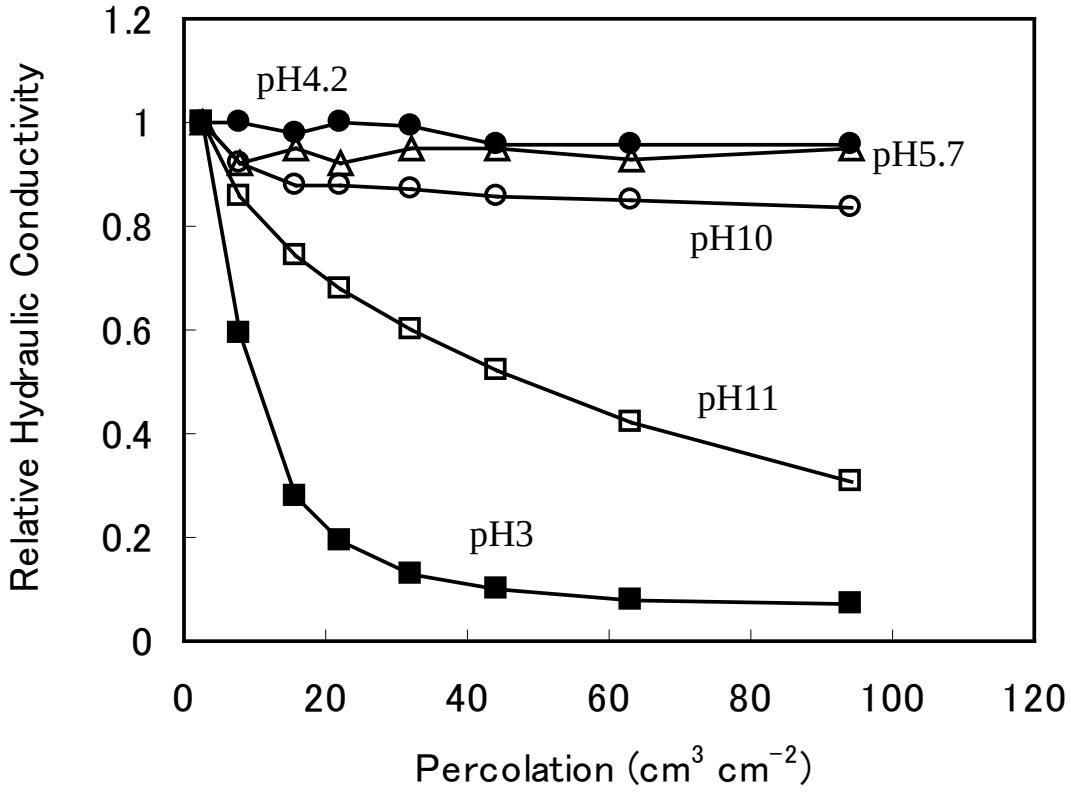


(a) Sr^{2+}



(b) Br-

Fig. 1



158

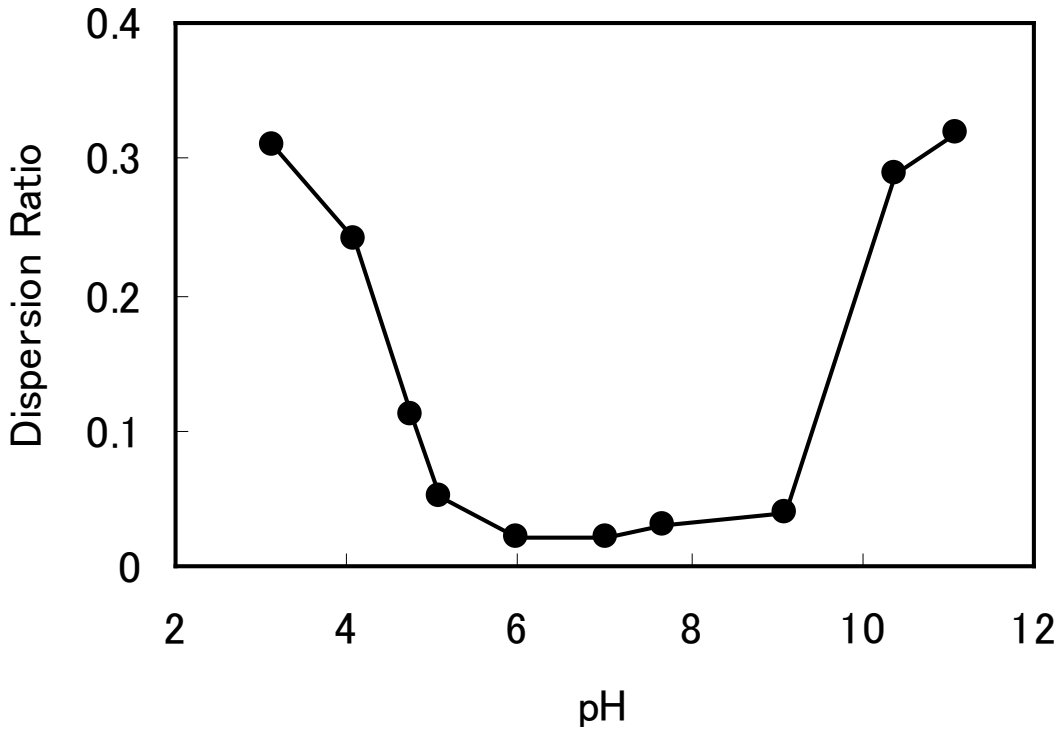
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162 Fig.2

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168 Fig.3
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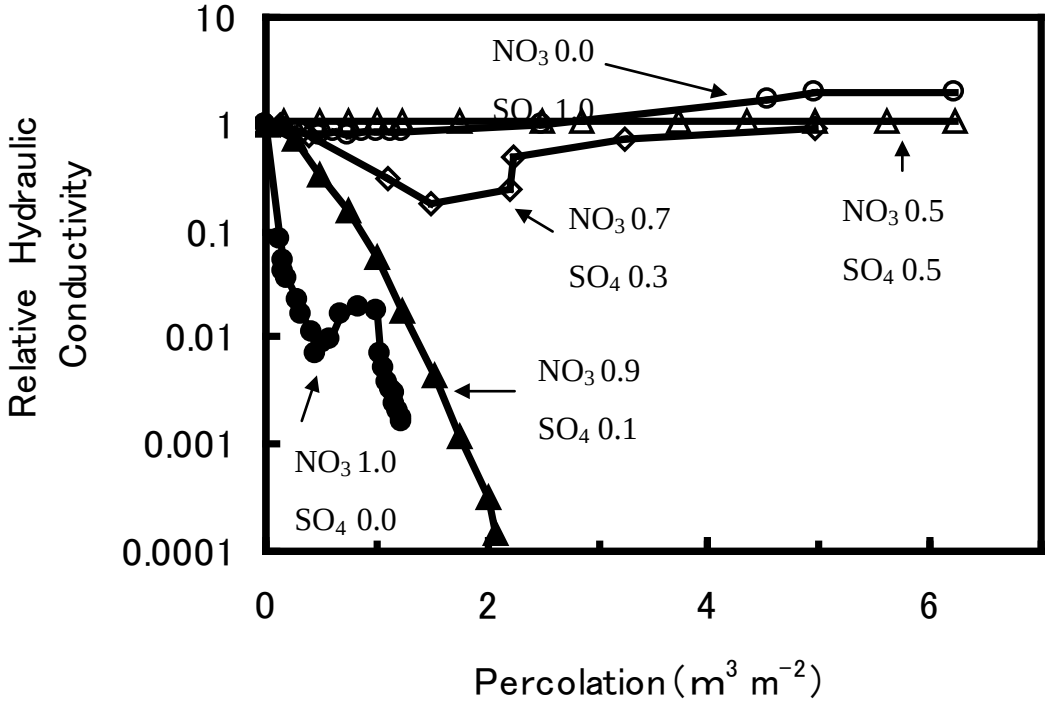
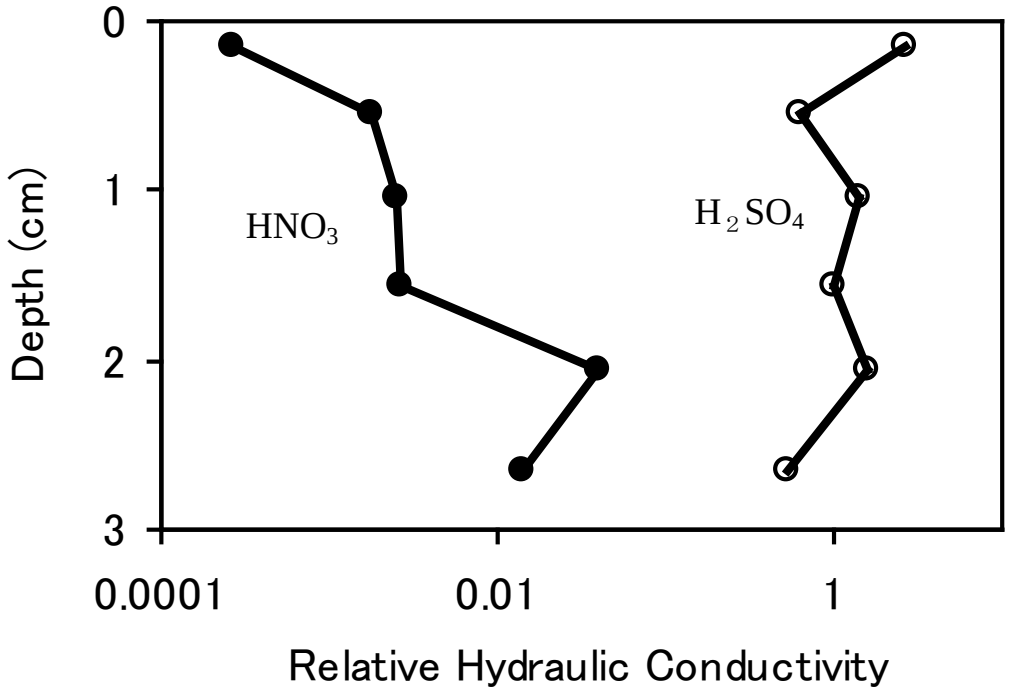

10
1
0.1
0.01
0.001
0.0001
Relative Hydraulic Conductivity
0
2
4
6
Percolation (m3 m-2)
NO3 0.0
SO4 1.0
NO3 0.7
SO4 0.3
NO3 0.5
SO4 0.5
NO3 0.9
SO4 0.1
NO3 1.0
SO4 0.0

Fig. 4



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184 Fig.5

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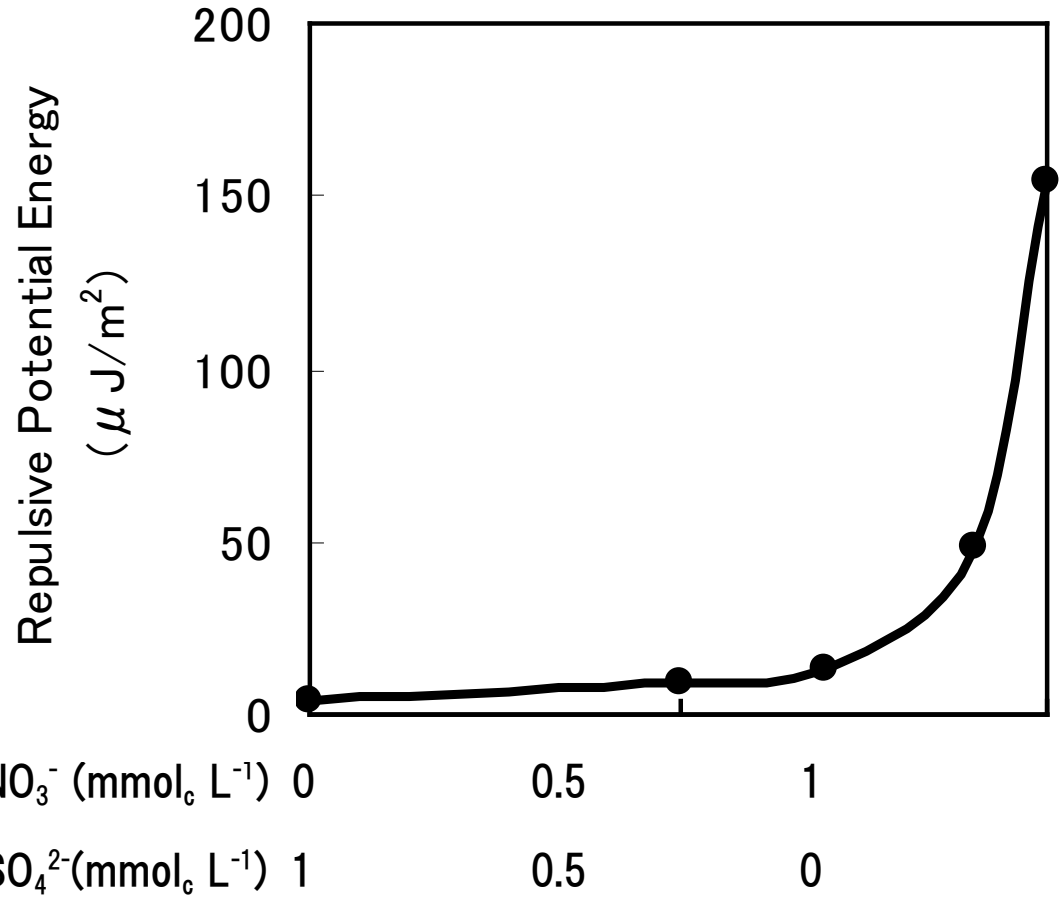

Repulsive Potential Energy
(μJ/m²)
200
150
100
50
0
NO3- (mmolc L-1) 0 0.5 1
SO4 2- (mmolc L-1) 1 0.5 0

Fig.6

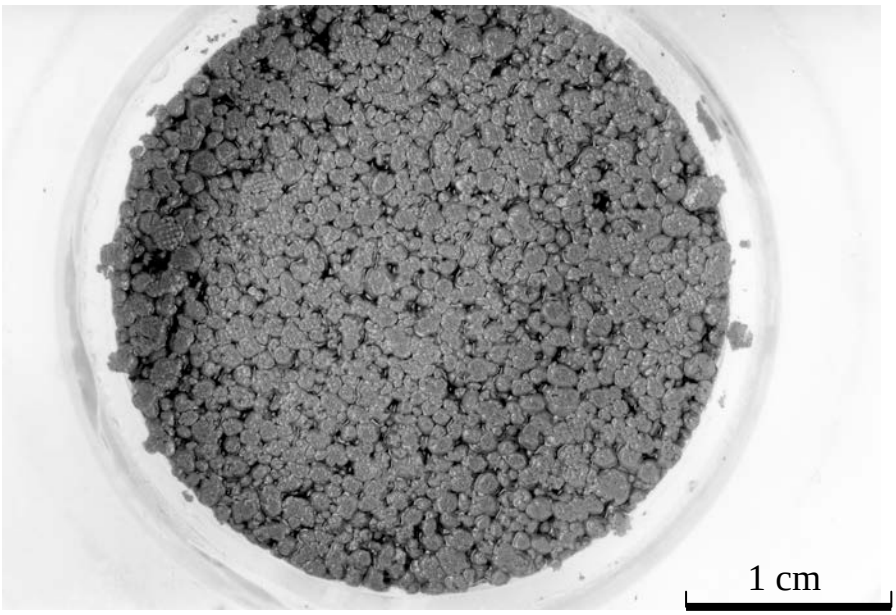


Photo 1 M. Ishiguro

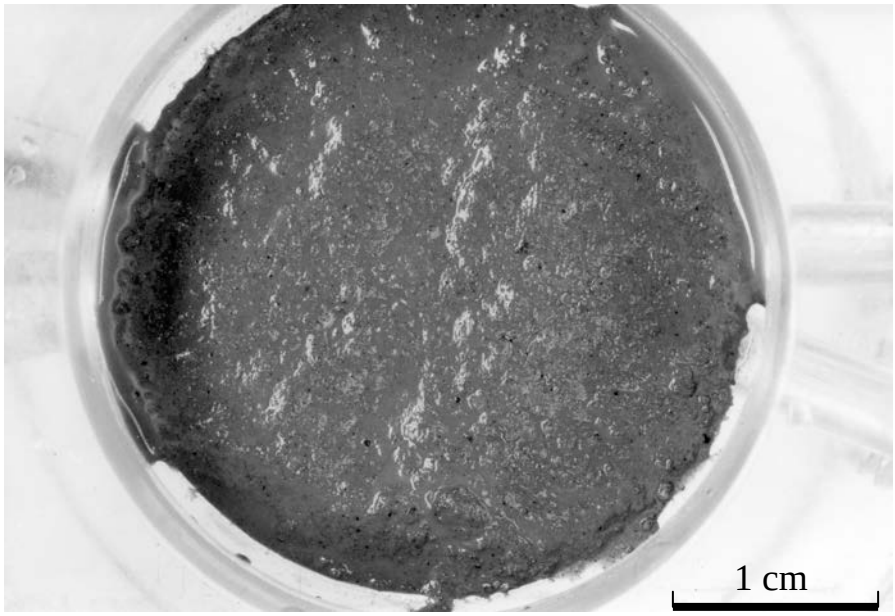


Photo 2 M. Ishiguro

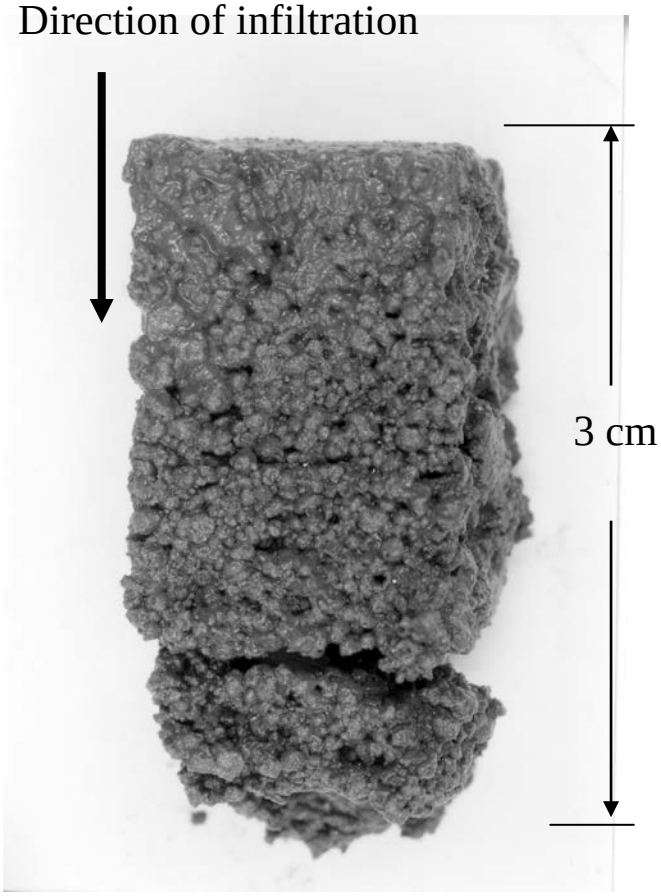


Photo 3 M. Ishiguro