



Title	Ion Transport and Permeability in an Allophanic Andisol at Low pH
Author(s)	Ishiguro, Munehide
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1 Ion Transport and Permeability in an Allophanic Andisol at Low pH

2 3 ABSTRACT

4
5 Allophanic Andisols have a significant pH-dependent charge. The positive charge increases
6 and the negative charge decreases as pH decreases; therefore, anion movement becomes slower
7 and cation movement becomes faster as pH decreases in the soil. At low pH, soil dispersion
8 occurs easily due to electric repulsive force. The permeability of the soil then decreases because
9 of structural changes that occur when dilute HCl or HNO₃ is percolated in the soil. However, soil
10 permeability does not decrease when dilute H₂SO₄ is percolated in the soil. This is because SO₄²⁻
11 strongly adsorbs on the soil surface at low pH and the soil remains flocculated.

12
13 **Keywords:** ion transport, permeability, allophanic Andisol, soil dispersion, flocculation.

14 15 INTRODUCTION

16
17 Charge characteristics of soils are important because they strongly influence ion transport and
18 soil structures. Commonly, soils possess pH dependent charges. Then, their effects are supposed
19 to be significant with pH change. However, few studies on the effects of solution pH on miscible
20 displacement experiment for exchanging ions have been reported (Chan et al. 1978; Chan et al.
21 1980a,b; Nielsen et al. 1986; Ishiguro et al. 1992). Studies on permeability change influenced by
22 pH have been also few (Suarez et al. 1984; Chiang et al. 1987; Nakagawa and Ishiguro 1994,;
23 Ishiguro et al. 2001). Allophanic Andisols, typical volcanic ash soils, have much amount of pH
24 dependent charge (Iimura 1966; Okamura and Wada 1983). In this paper, ion transport, soil
25 structure change and permeability change of the allophanic Andisol under low pH conditions
26 were investigated and integrated the former researches.

27 28 MATERIALS AND METHODS

29
30 **Soil.** An allophanic Andisol (Hapludand) was obtained from a field at the National Institute

31 of Agro-Environmental Sciences in Tsukuba, Japan, from a depth of approximately 90 cm (4Bw1
32 horizon). The predominant clay minerals were allophane and imogolite. The sand content was
33 130 g kg^{-1} , silt content was 375 g kg^{-1} , and clay content was 495 g kg^{-1} . The organic C content was
34 11.6 g kg^{-1} . The <2-mm sieved field moist soil was used in all experiments. As pH decreased, the
35 cation exchange capacity (CEC), the negative charge of the soil, decreased, and the anion
36 exchange capacity (AEC), the positive charge of the soil, increased. Both the CEC and the AEC
37 increased with an increase in ion strength.

38 **Miscible displacement experiment.** Sr^{2+} and Br^- breakthrough curves were obtained from
39 saturated soil column tests. An acrylic column 30-cm long and 6.5-cm inside diameter (ID) was
40 used. The hydraulic gradient was maintained at 0.5 m m^{-1} . A SrBr_2 solution at $0.01 \text{ mol}_c \text{ L}^{-1}$ at
41 prescribed pH (pH 5.05, pH 5.75 or pH 7.2) was percolated into soil columns with the same pH
42 condition (pH 5.05, pH 5.75 or pH 7.2) that had been initially saturated with a CaCl_2 solution at
43 $0.01 \text{ mol}_c \text{ L}^{-1}$ at prescribed pH (pH 5.05, pH 5.75 or pH 7.2). Influent pH and effluent pH were
44 same during this experiment. Sr^{2+} was analyzed by atomic absorption spectroscopy. Br^- was
45 measured by ion chromatography.

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

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

57

58 RESULTS AND DISCUSSION

59

60 **Miscible displacement experiment**

Fig.1

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

Fig.2

67 **Hydraulic conductivity study under different pH conditions**

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

Photo 1, 2, 3

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

Fig.3

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

Figs.4, 5

87 **Hydraulic conductivity study at pH 3**

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

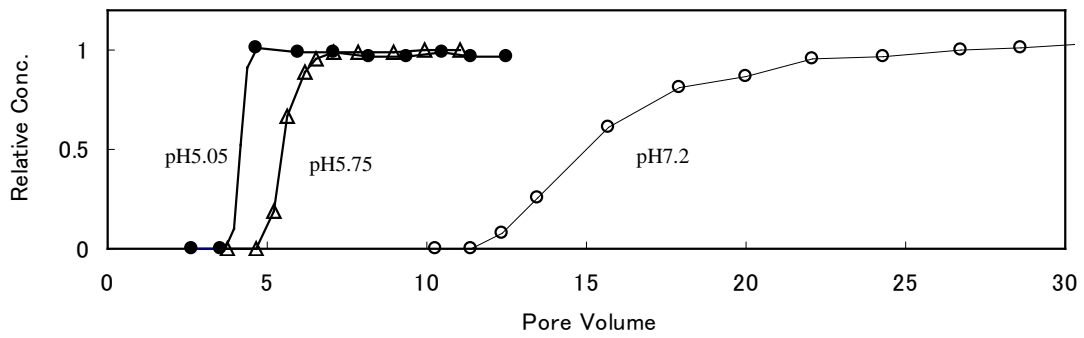
103 The electric repulsive potential energy between soil clay particles in mixtures of HNO_3 and
104 H_2SO_4 at pH 3 was calculated using the Gouy-Chapman theory (Ishiguro et al. 2003) and
105 electrophoretic mobility data as shown in Fig. 6. The horizontal axis in Fig. 6 indicates the
106 concentrations of NO_3^- and SO_4^{2-} ($\text{mmol}_c \text{L}^{-1}$) 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 $1 \text{ mmol}_c \text{L}^{-1}$ 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).

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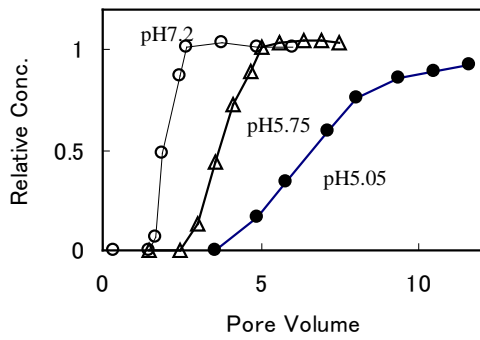
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(a) Sr²⁺



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(b) Br⁻

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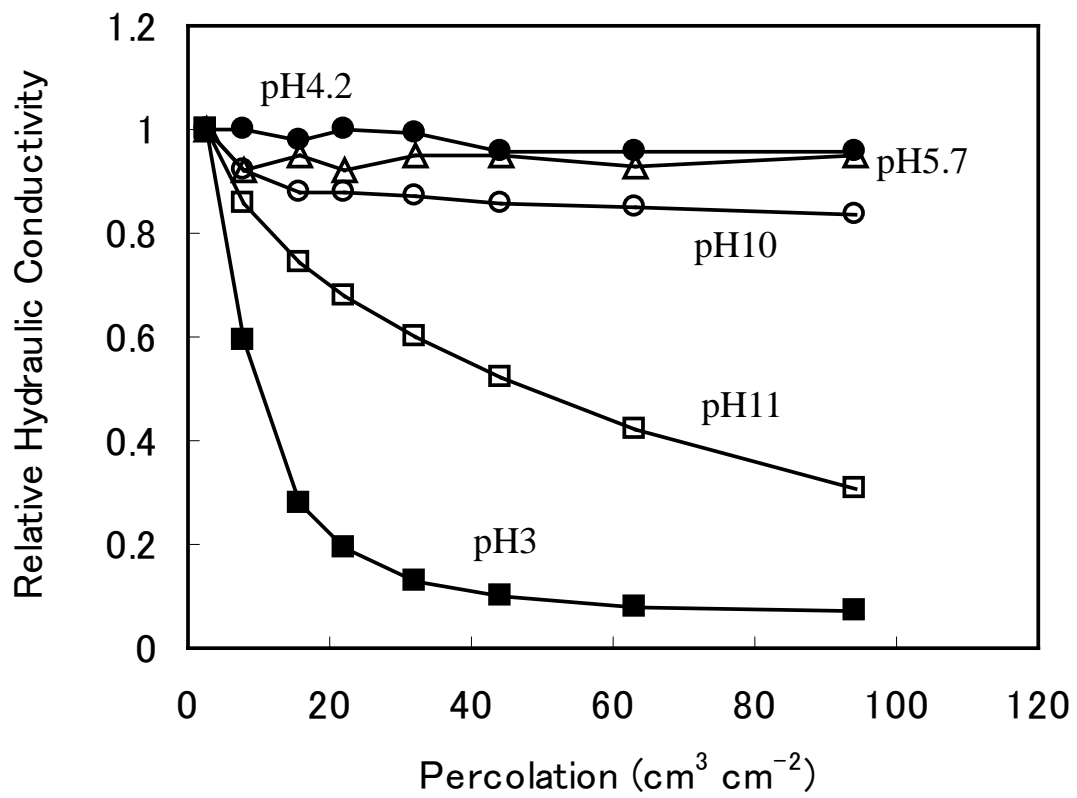
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155 Fig. 1

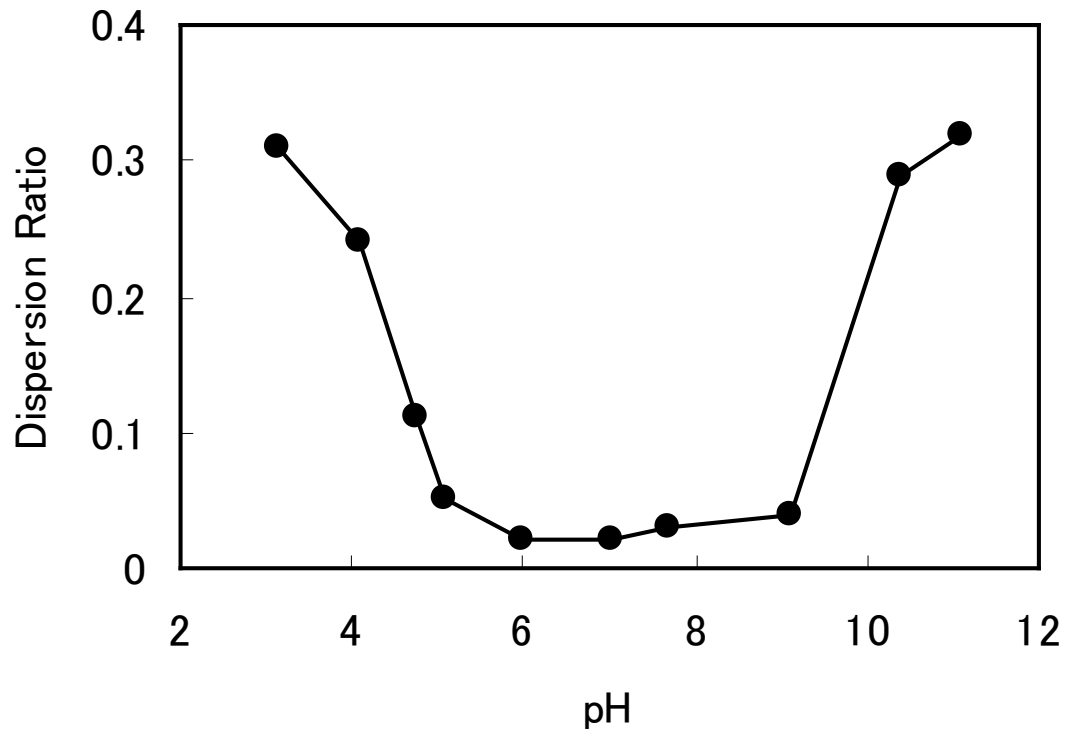
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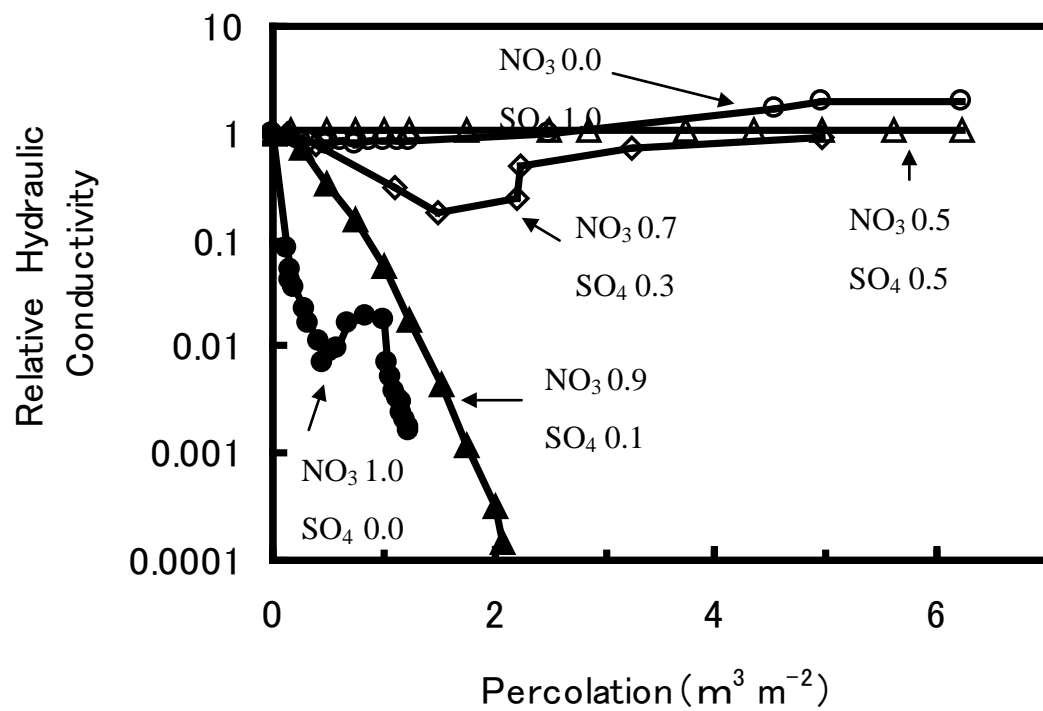
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Fig.2



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Fig.3



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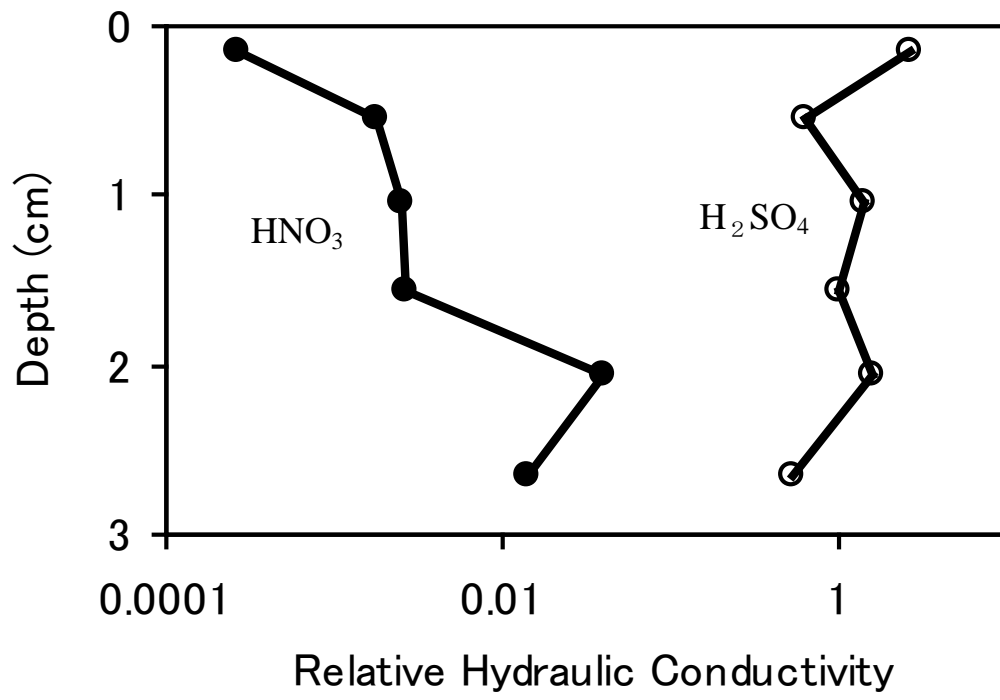
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178 Fig. 4

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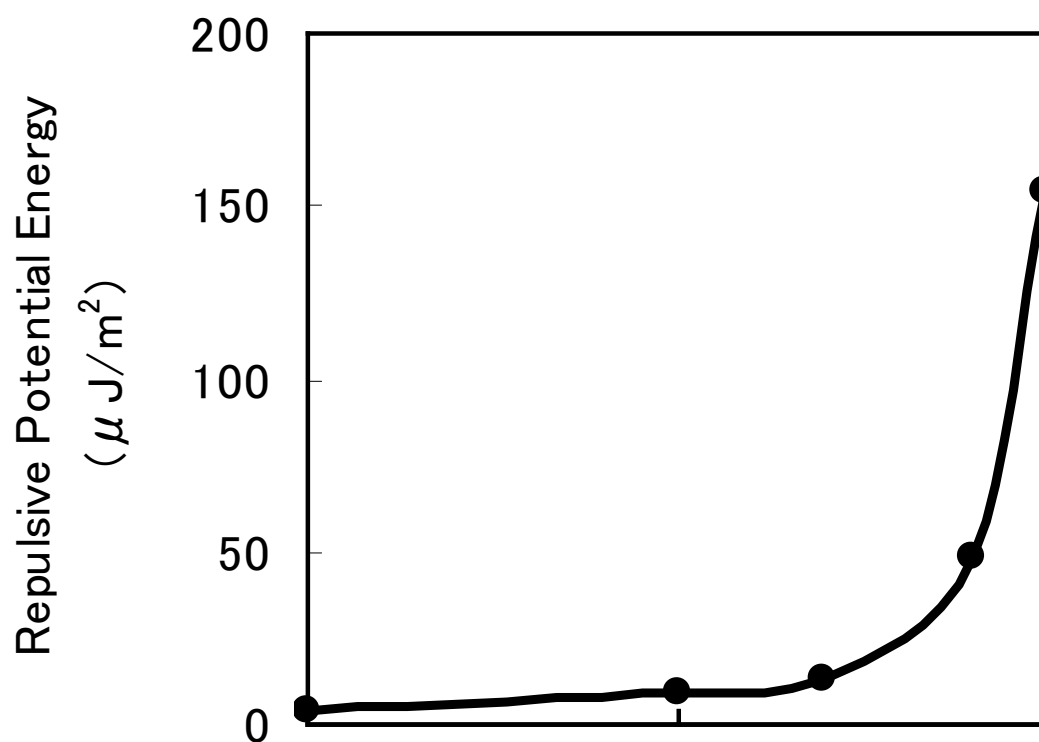
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184 Fig.5

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186 NO_3^- (mmol_c L⁻¹) 0 0.5 1

187 SO_4^{2-} (mmol_c L⁻¹) 1 0.5 0

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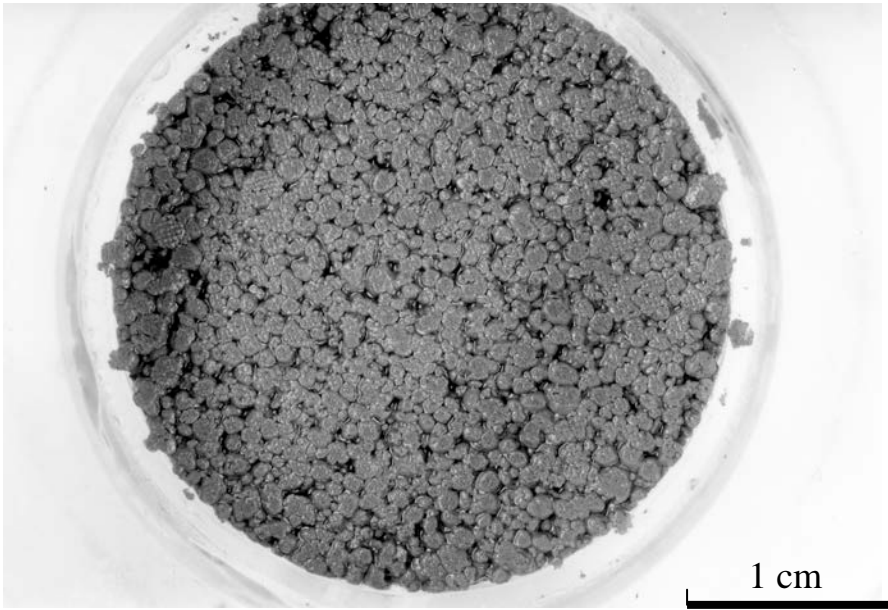
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194 Fig.6

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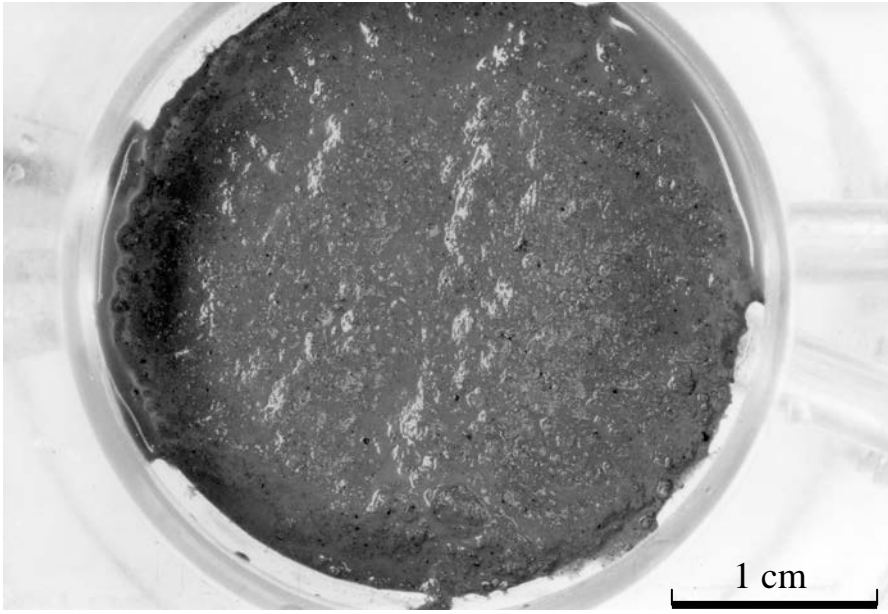
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214 Photo 1 M. Ishiguro

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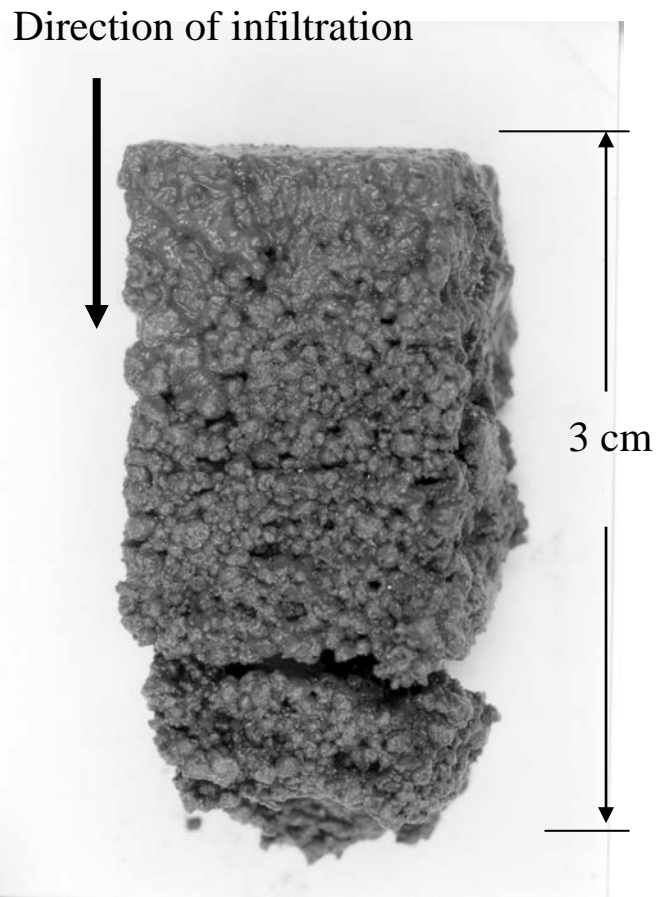
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234 Photo 2 M. Ishiguro

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244 Photo 3 M. Ishiguro

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