

Effectiveness of adsorption layer using natural volcanic ash in reducing arsenic leached from mudstone



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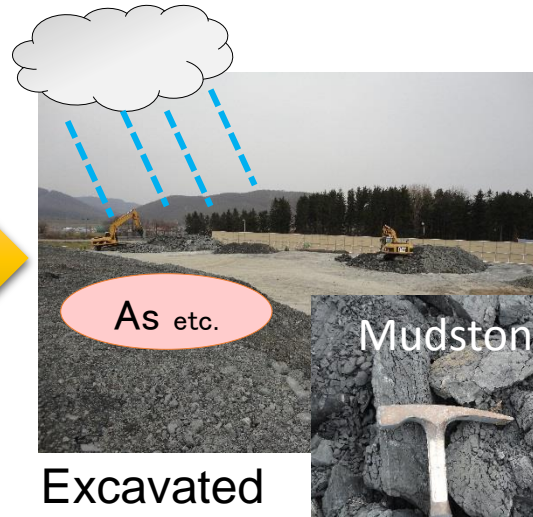
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Tunnel construction



Excavated rocks



Heavy metals

- Heavy metals and metalloids (*As etc.*) leach from excavated rocks.
→ Risk of contamination of the surrounding soil and groundwater
→ Countermeasures are needed.

- Although **impermeable layers**, such as geomembrane and clay, have been generally utilized as countermeasures against these kinds of rocks to isolate them from the surrounding environment in Japan, **the cost is very expensive.**



Impermeable layers



More economical and sustainable alternative methods are required.

➤ *Ubiquitous Material*

Volcanic ash



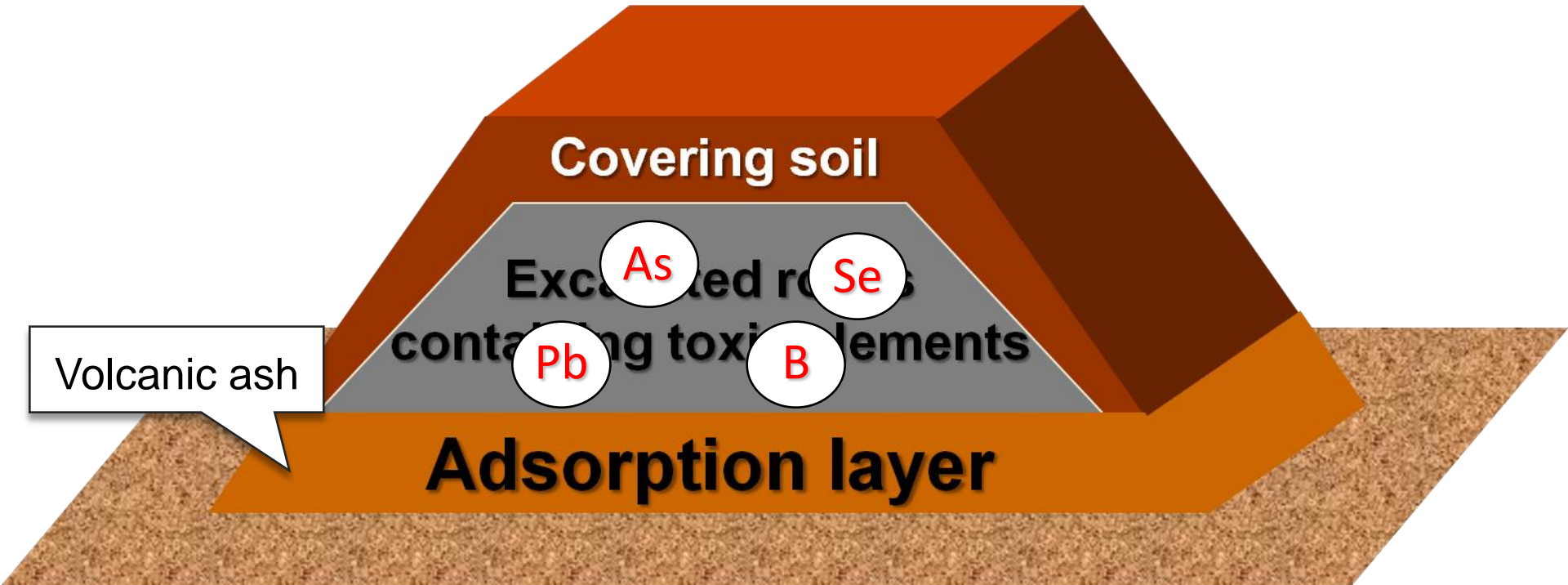
□ is cheap and abundant.

□ contains significant amounts of amorphous mineral with aluminum (Al) and iron (Fe) oxides/oxy hydroxides.

□ has high uptake of various heavy metals.

□ is a potentially effective adsorbent.

➤ Reasonable countermeasures: Adsorption layer system



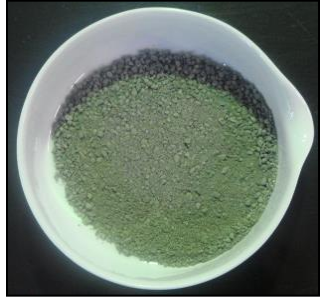
Objective of this study

To understand the adsorption characteristic of the volcanic ash layer against toxic elements leached from crushed rocks.

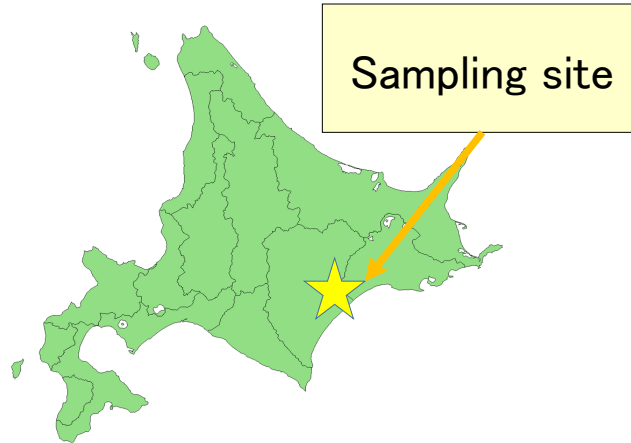
Materials

(Excavated rock used in this study)

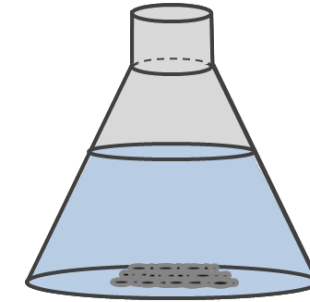
Excavated rocks
(Mudstone)



Hokkaido



Batch experiment



To mix 20 g of sample with
200 mL of distilled water
and shake for 6 hr at 200 rpm

Table 1. The results of batch leaching experiments.

Elements	As	SO ₄ ²⁻	Ca ²⁺	Na ⁺	pH
Leaching concentration (mg/L)	0.008	38.5	44.1	44.1	10.8
Environmental standard (mg/L)	0.01	-	-	-	6.50-8.50

Table 2. Chemical composition of the rock (Results of XRF).

Element	SiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	P ₂ O ₅ (wt.%)	TiO ₂ (wt.%)	S (wt.%)	As (mg/kg)
Crushed rock	65.7	15.0	6.41	0.06	2.80	2.60	1.70	3.54	0.16	0.72	0.24	10.0

As leaching from excavated rock is the focus.

Materials (Volcanic ash used in this study)

Volcanic ash



Acidic oxalate solution extraction

To mix 1 g of ash sample with 100 mL of acidic oxalate solution and shake for 4 hr at 120 rpm

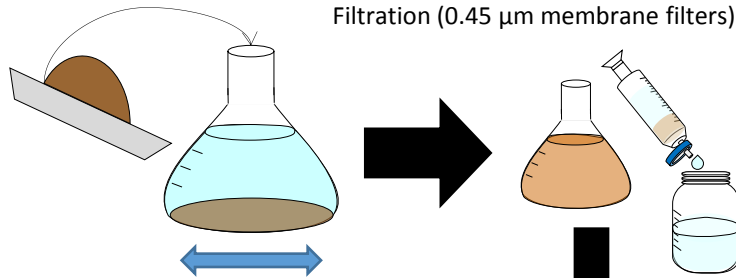
Amorphous Al and Fe

Al: 32 mg/g
Fe: 10 mg/g

✓ In order to detect the amorphous Al and Fe contents

Batch adsorption experiments

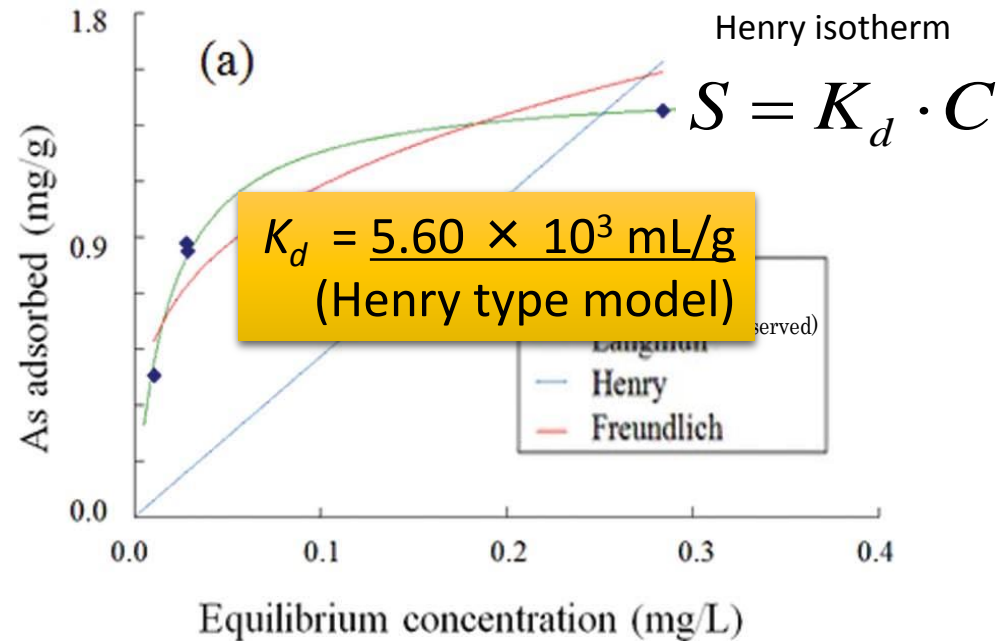
Volcanic ash + As (V) solution: 1.0 mg/L



Filtration (0.45 µm membrane filters)

Solid-Liquid ratio:
1:200, 1:500, 1:1000, 1:2000
120 rpm
Shaking time: 24 h

Quantitative analysis of As etc.



✓ In order to describe the adsorption isotherms of As and determine the K_d value

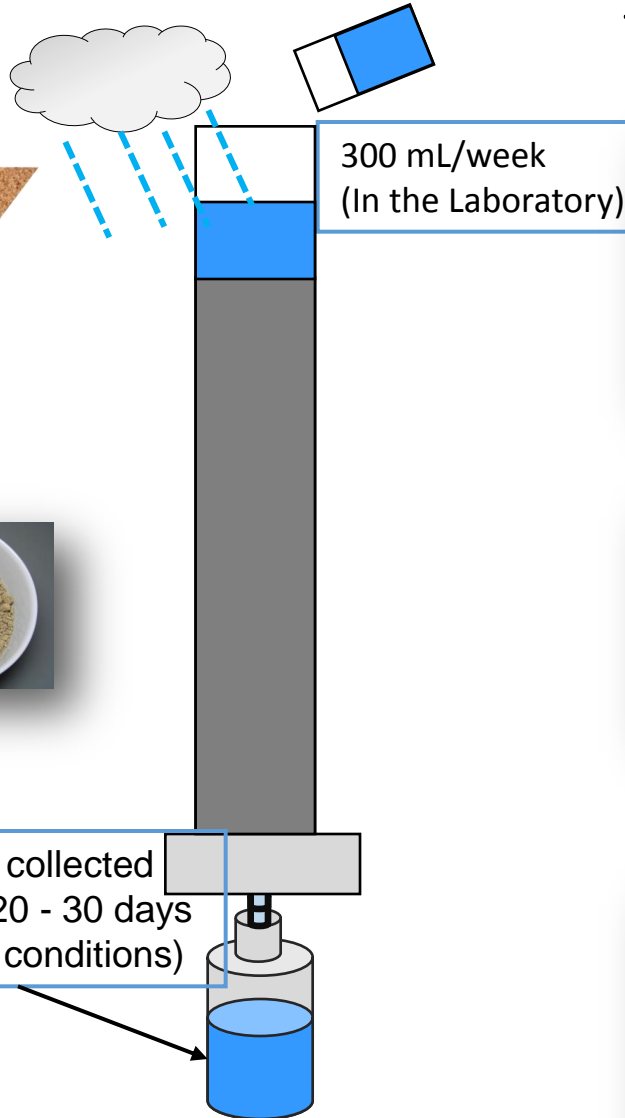
Column Experiments

Adsorption layer system

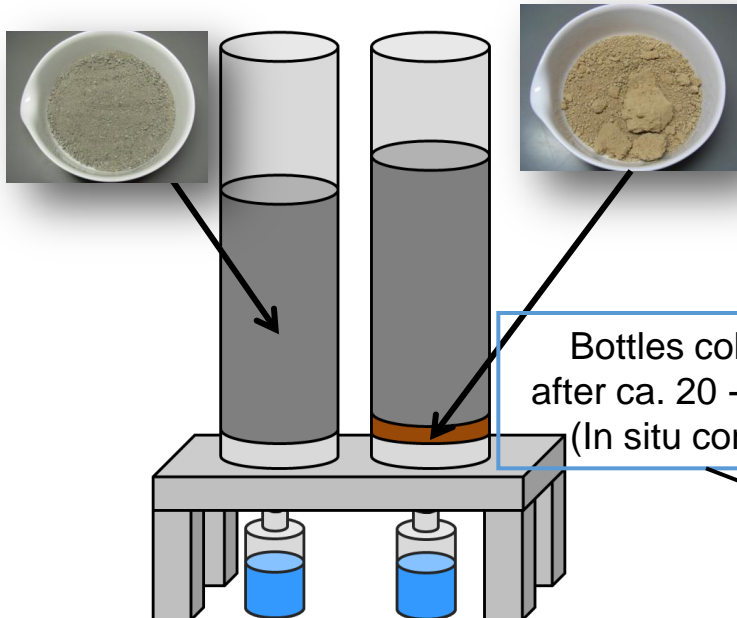


Procedures of column experiments

To measure some parameters (e.g., pH)



Column experiments



Filtration



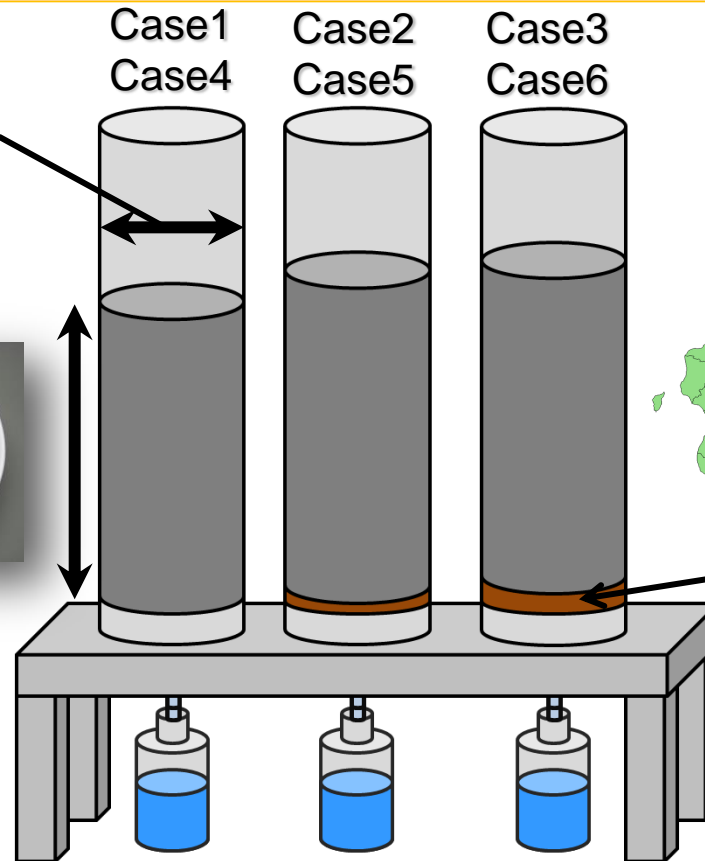
Analysis of the As concentration



The Case of Column Experiments

10.5 cm (Laboratory)
29.8 cm (In situ conditions)

Rock sample



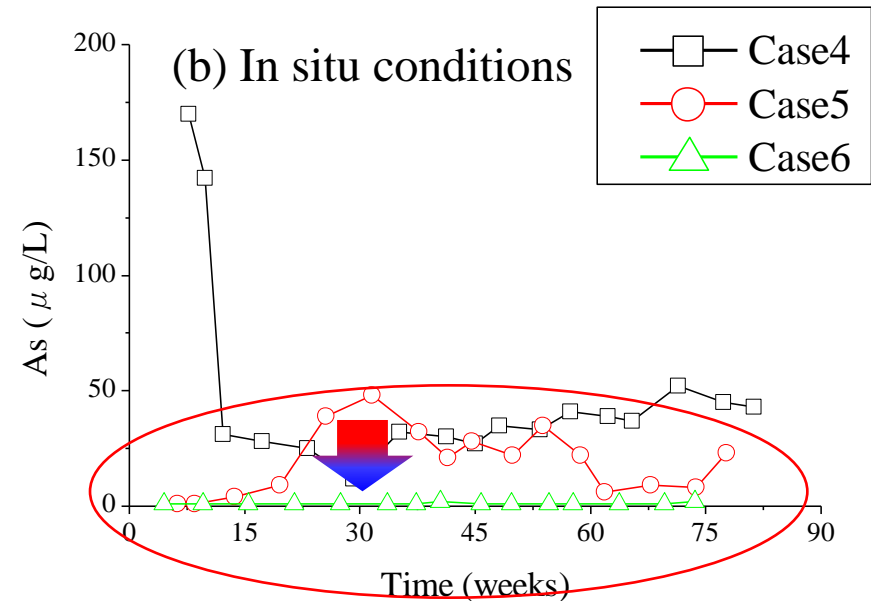
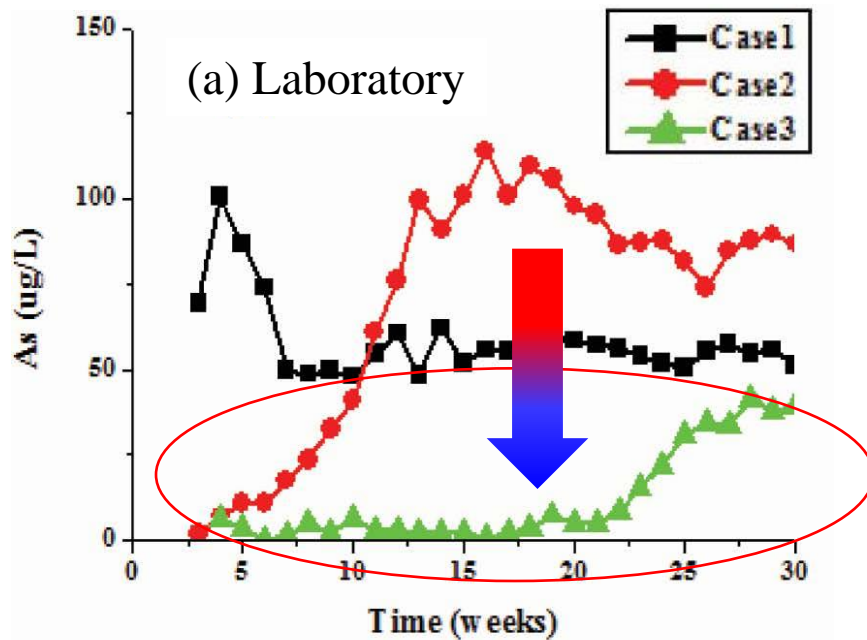
In situ
experiments site

Volcanic ash



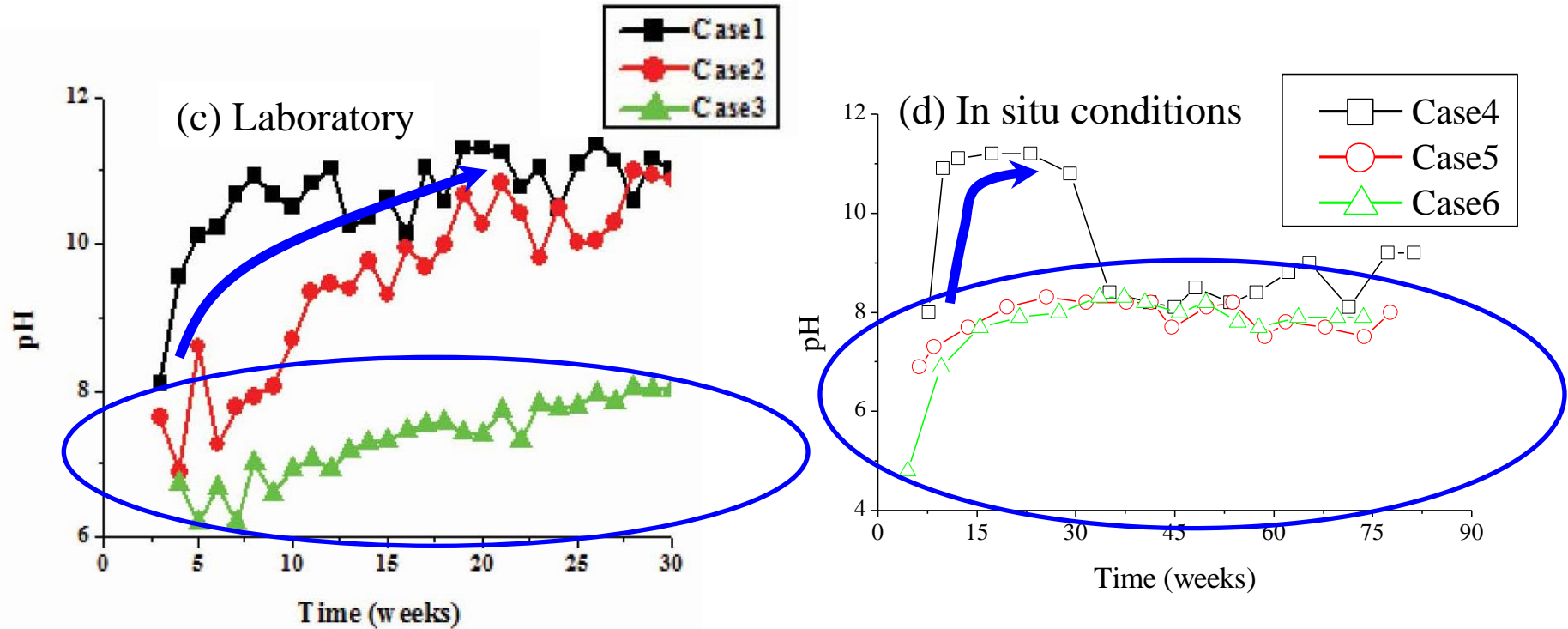
Cases	Location	The thickness of rock sample (cm)	The thickness of volcanic ash (cm)	Experiment periods (weeks)
1	Laboratory	30	0	30
2	Laboratory	30	1	30
3	Laboratory	30	2	30
4	in situ	60	0	82
5	in situ	60	2	78
6	in situ	60	6	74

Breakthrough curves of As



- The volcanic ash layer reduced As concentration of the leachate.
- Retardation of As migration was observed due to adsorption by the volcanic ash.
- Increasing the thickness of the ash layer resulted in a longer delay and lower maximum concentration of As released from the rock.

Breakthrough curves of pH



In cases 1 and 4,

The leachate from the rock sample was hyperalkaline.

→ The presence of calcite and smectite increased pH around 11 when in contact with water.

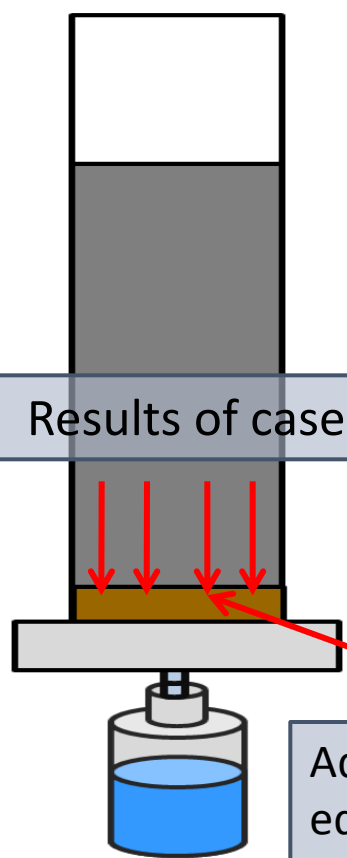
By setting the bottom volcanic ash layer,

The pH decreased to around 5 to 7 at the beginning of the experiments in cases 2, 3, 5 and 6, then increased gradually.

→ This is due to the interactions of the hyperalkaline leachate from the crushed rock and minerals such as a basaltic glass in the volcanic ash.

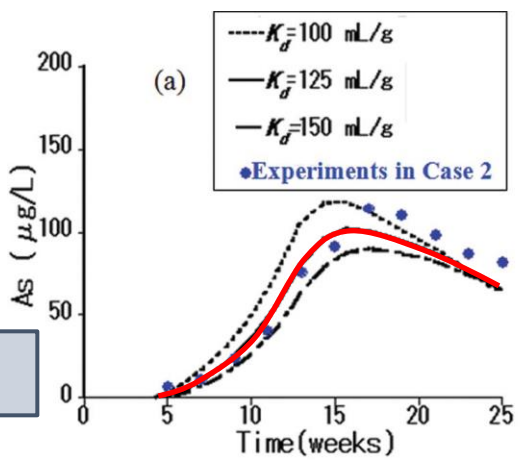
Simulation of As migration in cases 2 and 5

The ASEAN++2013

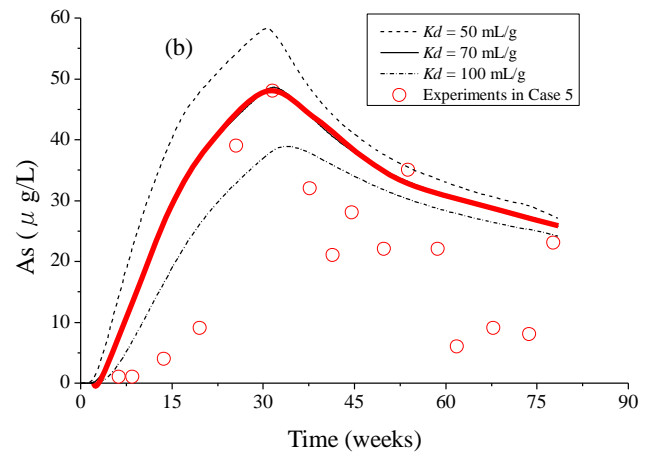


Results of cases 1 and 4

Advective-dispersive equation with Henry type adsorption model



(a) Laboratory
 $K_d = 125 \text{ mL/g}$



(b) In situ conditions
 $K_d = 70 \text{ mL/g}$

Calculated results agreed well with the experimental results.



This indicates that the Henry type model can evaluate the adsorption behavior of As.

- The bottom adsorption layer was **effective in retaining As** and could be used for the disposal of the excavated rock.
- By increasing the thickness of the volcanic ash layer, **the reduction of As leaching concentrations and the delay of its migration** were enhanced.
- The As migration can be simulated using advective - dispersive equation with Henry type adsorption model.

***Thank you
for your attention.***

Experimental part

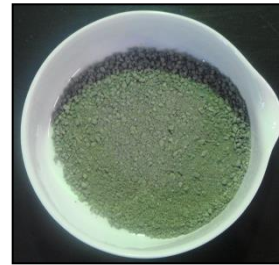
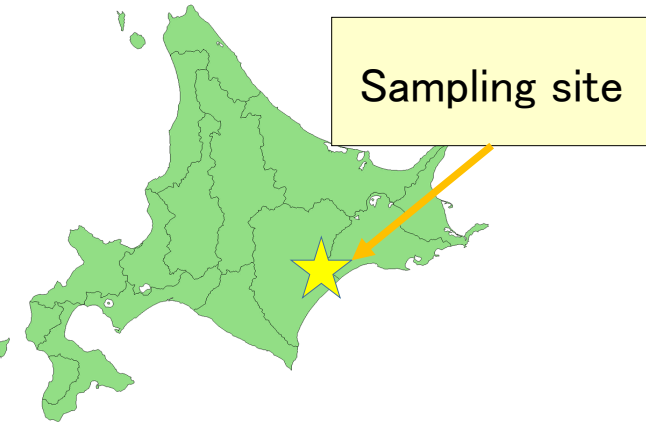
- ✓ Column experiments in the laboratory and in the in situ
 - To understand the concentrations and leaching behaviors of As and pH.

Simulation part

- ✓ Numerical analysis using the one-dimensional advective-dispersive equation
 - To evaluate the effects of the adsorption layer on the mobility of As.

Materials (Characterization of the rock sample)

- The mudstone sample was obtained from a tunnel construction site in the island of Hokkaido, Japan.
- The sample was air-dried, crushed, and sieved using a 2 mm aperture screen.



Mudstone

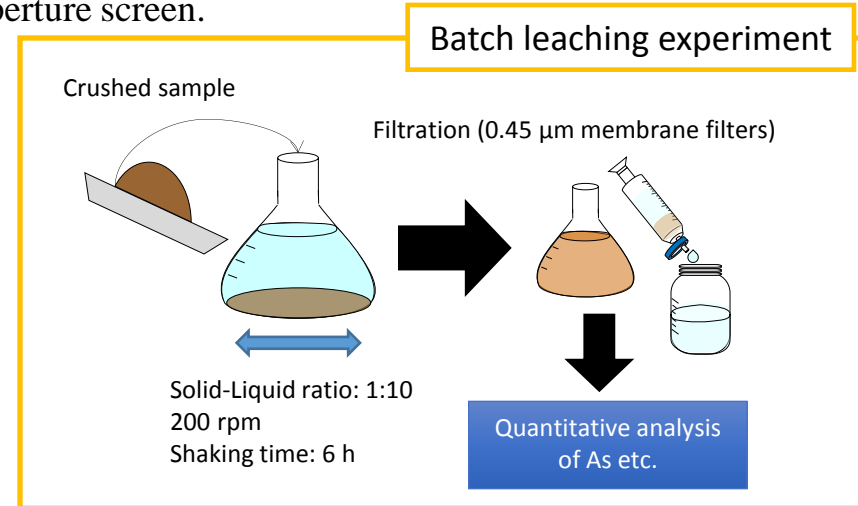


Table 1. Mineral composition of the rock (Results of XRD).

Mineral	Quartz	Feldspar	Calcite	Mica	Chlorite	Smectite	Pyrite
Crushed rock	+++	++	+	+	+	+	±

+++: strong, ++: moderate, +: weak, ±: trace, -: none

Table 2. Chemical composition of the rock (Results of XRF).

Element	SiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	P ₂ O ₅ (wt.%)	TiO ₂ (wt.%)	S (wt.%)	As (mg/kg)
Crushed rock	65.7	15.0	6.41	0.06	2.80	2.60	1.70	3.54	0.16	0.72	0.24	10.0

Table 3. The results of batch leaching experiments.

Elements	As	SO ₄ ²⁻	Ca ²⁺	Na ⁺	pH
Leaching concentration (mg/L)	0.008	38.5	44.1	44.1	10.8
Environmental standard (mg/L)	0.01	-	-	-	6.50-8.50

Materials (Characterization of volcanic ash)

- The volcanic ash sample used for the adsorption layer was collected near the tunnel construction site.
- The sample was dried and sieved to obtain less than 2 mm in diameter.

Table 4. Mineral composition of the rock (Results of XRD).

Mineral	Quartz	Feldspar	Calcite	Mica	Chlorite	Smectite	Pyrite
Volcanic Ash	+++	++	-	-	+	-	-

+++: strong, ++: moderate, +: weak, ±: trace, -: none

Table 5. Chemical composition of the rock (Results of XRF).

Element	SiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	P ₂ O ₅ (wt.%)	TiO ₂ (wt.%)	S (wt.%)	As (mg/kg)
Volcanic Ash	52.6	24.0	10.3	0.21	1.70	3.30	0.24	1.09	0.17	0.95	0.05	12.0

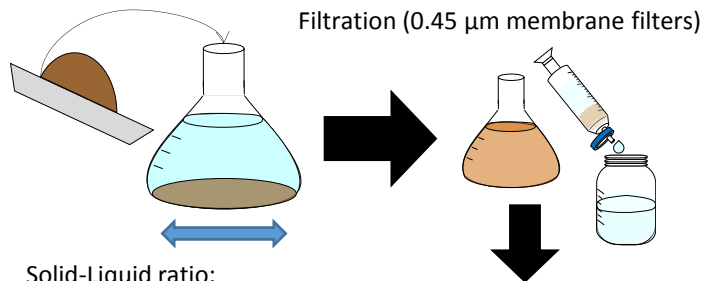


Volcanic ash

Amorphous Al and Fe → Al: 32 mg/g
Fe: 10 mg/g

Batch adsorption experiment

Volcanic ash + As (V) solution: 1.0 mg/L

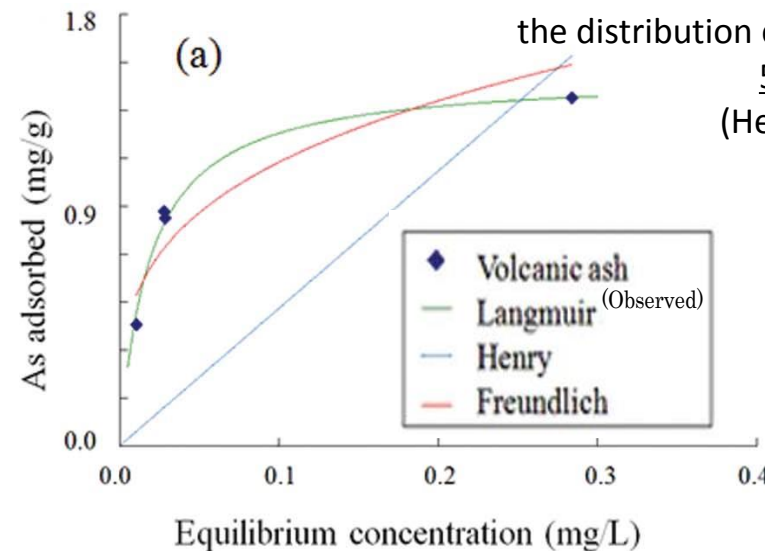


Solid-Liquid ratio:
1:200, 1:500, 1:1000, 1:2000
120 rpm
Shaking time: 24 h

Quantitative analysis of As etc.

$$q = \frac{(C_0 - C) \cdot V}{W}$$

where,
q: the adsorbed amount
C₀: the initial concentration
C: the equilibrium concentration, V: the volume of solution, W: the amount of volcanic ash added



the distribution coefficient of As:
 5.60×10^3 mL/g
(Henry type model)

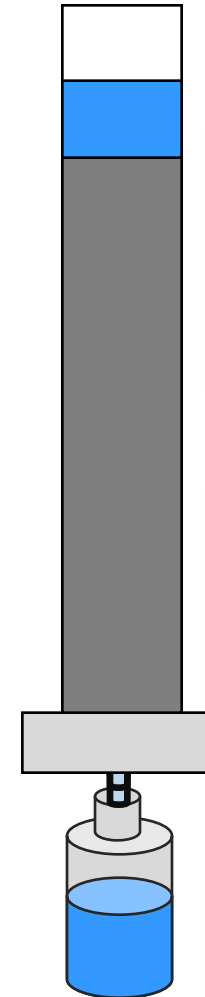
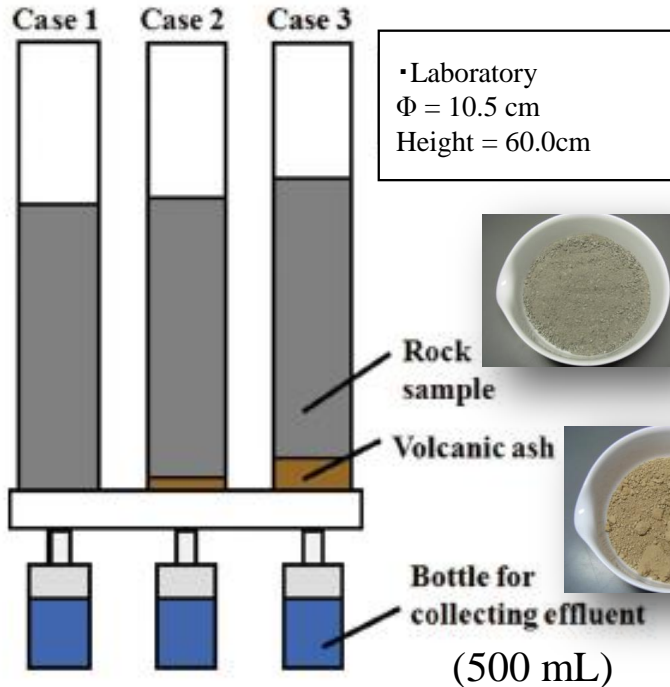
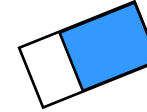
Fig. 1 The adsorption isotherms of volcanic ash for As.

where, q: the adsorbed amount, C₀: the initial concentration, C: the equilibrium concentration, V: the volume of solution, W: the amount of volcanic ash added

Experimental procedure The ASEAN++2013

➤ Column experiments in the laboratory

300 mL/week



To measure some parameters (e.g., pH)



Filtration (0.45 μm MF)



Analysis of the As concentration



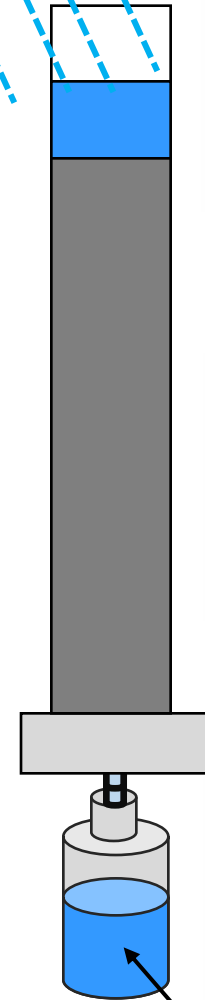
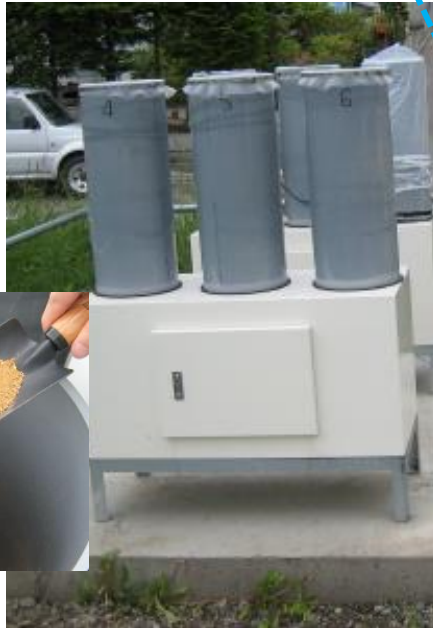
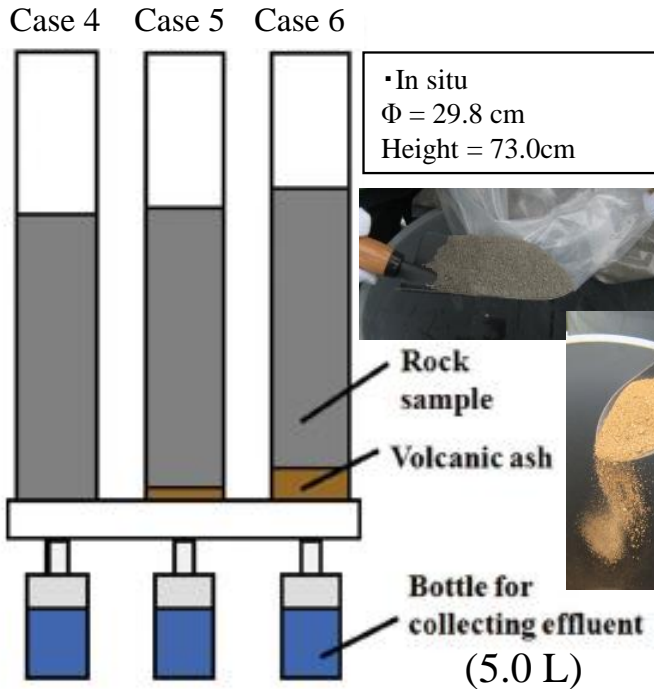
Table 6. The cases of the column experiments in the laboratory

Cases	Location	The thickness of rock sample (cm)	The thickness of volcanic ash (cm)	Experiment periods (weeks)
1	Laboratory	30	0	30
2	Laboratory	30	1	30
3	Laboratory	30	2	30

The crushed rock and volcanic ash samples were compacted to adjust the bulk densities to 1.28 and 0.72 g/cm³.

Experimental procedure The ASEAN++2013

➤ Column experiments in situ conditions



Filtration (0.45 μm MF)



To measure some parameters (e.g., pH)



Analysis of the As concentration



Table 7. The cases of the column experiments in situ conditions

Cases	Location	The thickness of rock sample (cm)	The thickness of volcanic ash (cm)	Experiment periods (weeks)
4	in situ	60	0	82
5	in situ	60	2	78
6	in situ	60	6	74

The crushed rock and volcanic ash samples were compacted to adjust the bulk densities to 1.58 and 1.72 g/cm³.

Bottles collected after ca. 20 - 30 days.

Advective-dispersive equation

$$\frac{\partial C}{\partial t} + \bar{v} \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2}$$

where,

C : solute concentration, t : time, \bar{v} : the average pore-water velocity, x : the depth, D : the dispersion coefficient.

Advective-dispersive equation with Henry type model

$$\frac{\partial C}{\partial t} + \frac{\bar{v}}{R_f} \frac{\partial C}{\partial x} = \frac{D}{R_f} \frac{\partial^2 C}{\partial x^2} \quad R_f = 1 + \frac{\rho_b}{\theta} K_d$$

Analytical solution

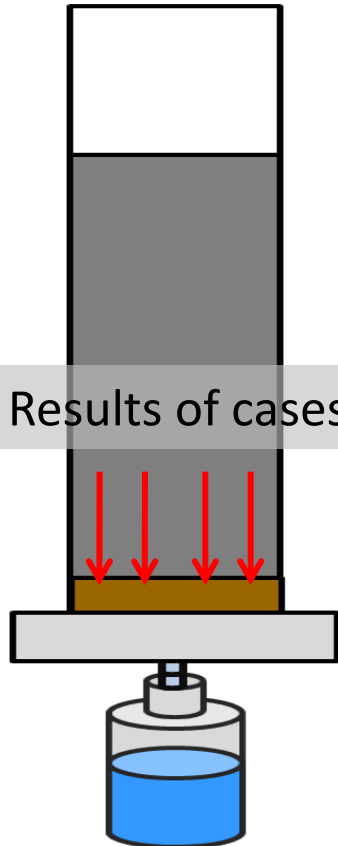
$$\frac{C(x,t)}{C_o} = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{R_f x - \bar{v}t}{2\sqrt{R_f D t}} \right) + \exp \left(\frac{\bar{v}x}{D} \right) \operatorname{erfc} \left(\frac{R_f x + \bar{v}t}{2\sqrt{R_f D t}} \right) \right\}$$

where,

C_o : the input concentration, R_f : the retardation factor, ρ_b : the bulk density, θ : the volumetric water content, K_d : the distribution coefficient

Case 2: $D = 1.00 \text{ cm}^2/\text{day}$, $\bar{v} = 100 \text{ cm/day}$

Case 4: $D = 4.00 \text{ cm}^2/\text{day}$, $\bar{v} = 1.20 \text{ cm/day}$



Results of cases 1 and 4