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Effects of Environmental Factors on the Leaching and Immobilization Behavior of Arsenic from Mudstone by Laboratory and In Situ Column Experiments

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Abstract: Hydrothermally altered rocks generated from underground/tunnel projects often produce acidic leachate and release heavy metals and toxic metalloids, such as arsenic (As). The adsorption layer and immobilization methods using natural adsorbents or immobilizer as reasonable counter-measures have been proposed. In this study, two sets of column experiments were conducted, of which one was focused on the laboratory columns and other on the in situ columns, to evaluate the effects of column conditions on leaching of As from excavated rocks and on adsorption or immobilization behavior of As by a river sediment (RS) as a natural adsorbent or immobilizer. A bottom adsorption layer consisting of the RS was constructed under the excavated rock layer or a mixing layer of the excavated rock and river sediment was packed in the column. The results showed that no significant trends in the adsorption and immobilization of As by the RS were observed by comparing laboratory and in situ column experiments because the experimental conditions did not influence significant change in the leachate pH which affects As adsorption or immobilization. However, As leaching concentrations of the in situ experiments were higher than those of the laboratory column experiments. In addition, the lower pH, higher Eh and higher coexisting sulfate ions of the leachate were observed for the in situ columns, compared to the results of the laboratory columns. These results indicate that the leaching concentration of As became higher in the in situ columns, resulting in higher oxidation of sulfide minerals in the rock. This may be due to the differences in conditions, such as temperature and water content, which induce the differences in the rate of oxidation of minerals contained in the rock. On the other hand, since the leachate pH affecting As adsorption or immobilization was not influenced significantly, As adsorption or immobilization effect by the RS were effective for both laboratory and in situ column experiments. These results indicate that both in situ and laboratory column experiments are useful in evaluating leaching and adsorption of As by natural adsorbents, despite the fact that the water content which directly affects the rate of oxidation is sensitive to weathering conditions.

Keywords: arsenic; in situ and laboratory experiments; adsorption layer; immobilization

1. Introduction

Rocks excavated from underground/tunnel projects have historically been considered as non-hazardous and are typically repurposed as embankment materials and aggregates for concrete during construction. In recent years, however, several studies reported that

certain types of rocks excavated from areas where hydrothermally altered rocks and sedimentary rocks of marine origin are distributed could potentially generate acidic and neutral leachate with similar geochemical properties as acid and neutral mine drainages (AMD/NMD) and/or continuously release hazardous trace elements to the environment, such as arsenic (As). In some cases, As leached from sedimentary rocks and igneous rocks exceeds 10 µg/L, which is the environmental standard in Japan [1–4]. The As content in igneous rocks is generally low, with an average value of 1.5 mg/kg for all igneous rock types [5]. The content of As in sedimentary rocks is typically between 5–10 mg/kg [6], slightly above average terrestrial abundance. Reported average background of As content in world soils is 7.2 mg/kg [7]. Arsenic is contained in minerals. The common minerals of As are realgar (As₄S₄), orpiment (As₂S₃), arsenopyrite (FeAsS), and enargite (Cu₃AsS₄) [8].

In Japan, for instance, several underground/tunnel construction projects on the island of Hokkaido in the last 15 years have excavated rocks which have released environmentally regulated elements, e.g., As, selenium (Se), boron, and lead [9]. Because of this, the bulk of excavated rocks are disposed of using the impermeable layer system, which is a similar system as sanitary landfill sites for industrial and municipal wastes [10]. Although this system is reliable for retaining hazardous elements contained in the rocks, it is costly and unsustainable because of the huge amounts of rocks excavated, so alternative and more reasonable disposal approaches are required.

Mudstones containing hazardous and mobile contaminant are not only a challenge in underground space development but also in mining and mineral processing operations [11]. In coal mining, for example, the overburden or waste rocks are typically composed of marine sedimentary rocks like mudstones and sandstones [12,13]. As mining operations become more extensive due to the metal and material needs for the transition to clean energy, this environmental problem associated with excavated rocks will become more pervasive [14]. There are two important sources of contaminants in mudstones [15]: (1) pyrite, and (2) soluble salts. When the amount of pyrite in the rock is higher than carbonates, then AMD will likely be generated with time [16,17]. In contrast, NMD is formed when there are more carbonate minerals like calcite and dolomite in the rock than acid forming minerals like pyrite [18]. Potentially acid-forming mudstones can be managed by blending with neutralizers and or disposed of using encapsulation [19]. In contrast, NMD from mudstones is more challenging to manage and may require advanced water treatment technologies like ion-exchange, electro-dialysis, and reverse osmosis depending on the target contaminants for removal [11].

Arsenic, a toxic contaminant well-known for increasing the risks of developing various types of cancers in humans, is commonly encountered in NMD from sedimentary rocks like mudstones and sandstones [20]. Because NMDs have a pH of around 7–9, As mobility is very high because under these conditions, its oxyanions do not undergo precipitation reactions [15]. Adsorption is one of the most effective techniques for the removal of As between pH 7–9, so one promising approach for NMD-generating mudstones is the bottom adsorption layer system that sequesters and immobilizes arsenic using natural or artificial adsorbents [21–27].

Conventional batch leaching tests, based on Japanese Environmental Agency notification No. 46 (JLT46) (1991) are commonly employed to determine the leaching concentrations of target contaminants and identify whether excavated rocks are hazardous or not in Japan [2,15,28,29]. Meanwhile, equilibrium batch adsorption experiments are conducted to determine the adsorption capacities by natural adsorbents, such as volcanic ash, and artificial adsorbents, e.g., iron (Fe) oxide, manganese oxide, calcite, bismuth oxide, metal-based nanoparticles, magnetic Fe₃O₄, or sugarcane bagasse activated carbon composite, for hazardous elements [30–38]. Thermal treatment enhances the adsorption capacity of the adsorbent, e.g., charred dolomite. The charring process allows dissociation of the dolomite to calcium carbonate and magnesium oxide, which accelerates the process of arsenic oxide and arsenic carbonate precipitation [39]. These batch testing protocols are easy to conduct, but they often overestimate or underestimate both the leaching of hazardous elements

from the rocks and adsorption capacities of adsorbents, which makes them unstable for in situ conditions. This is because factors like leachant regeneration, solid-to-liquid ratio and water flow that control the long-term leaching and adsorption behaviors of hazardous elements are not captured by batch experiments [20].

An alternative to batch test protocols is column experiments, typically consisting of a crushed rock layer with and without a bottom adsorption layer packed into plastic pipes which demonstrates the effects of unsaturated-saturated water flow conditions prevalent under in situ conditions. In several studies, for example, column experiments and impoundment-type in situ experiments revealed that leaching behavior of hazardous elements from excavated rocks were strongly influenced by pH, oxidation-reduction potential (Eh), dissolved oxygen (DO), volumetric water content, coexisting ions produced by oxidation of sulfide minerals such as a pyrite, and precipitation of secondary minerals such as Fe oxide/oxyhydroxides [40–45]. Although in situ column experiments are effective in simulating the leaching and adsorption of hazardous elements under actual conditions, they require several years to complete, and the results are often too complex to interpret effectively [46]. To address these drawbacks, laboratory column experiments are promising alternatives because they are easy to conduct, and the infiltration rate could be adjusted to speed up the experiments. However, there have been few studies on the comparison between laboratory and in situ column experiments and the evaluation of the effects of experimental conditions on the leaching and adsorption of hazardous elements from excavated rocks. Hence, if the effects of the conditions between laboratory and in situ column experiments are insignificant for leaching and adsorption/immobilization behavior of hazardous elements, laboratory column experiments could become more effective for evaluating the leaching and adsorption/immobilization behavior of the elements under actual impoundment conditions.

In this study, two sets of column experiments were conducted in the laboratory and in situ to evaluate the leaching of As from the two types of excavated rocks excavated from tunnel projects. Moreover, the adsorption and immobilization of As by a natural adsorbent were elucidated by adding bottom adsorption layers or mixing the natural adsorbent with rock samples. The results obtained in this study will be effective in evaluating the leaching behavior of As and the adsorption and immobilization properties of As by the natural adsorbent in actual sites.

2. Materials and Methods

2.1. Rock Sample Collection and Characterization

Two mudstone samples were collected from different tunnel construction sites (T1 and T2 tunnels) in Hokkaido, Japan. Both tunnels traverse the Cretaceous-Paleocene Yeso basin, a 10,000 m thick forearc sedimentary sequence of sandstones and mudstones with subordinate conglomerate, that stretches northward from the offshore of northern Honshu through Hokkaido up to Sakhalin Island, Russia [47].

Our preliminary experiments showed that rocks used in this study had high leaching concentrations of As and slightly higher leaching concentration of Se than the environmental standard ($<0.010 \text{ mg/dm}^3$) [48]. Therefore, this paper focused on evaluating As leaching and adsorption/immobilization behavior. The previous study also clarified that As speciation leached from T1 and T2 samples were mainly arsenate (As (V)) with lower concentration of arsenite (As (III)) [49]. Thus, only total As (As(III) + As (V)) leaching and adsorption/immobilization behaviors were compared.

The rock sample was collected randomly from interim storage using hand shovels, air-dried in the laboratory, manually crushed and sized with a series of sieves.

Chemical and mineralogical compositions of the samples were determined using an X-ray fluorescence spectrometer (XRF) (Spectro Xepos, Rigaku Corporation, Japan) and an X-ray-diffractometer (XRD) (Multi Flex, Rigaku Corporation, Japan), respectively. For greater accuracy, the As content of the rocks were quantified by the wet method, a

procedure that involves the complete dissolution of samples with a mixture of concentrated hydrochloric, nitric and perchloric acids and subsequent analysis of the leachates.

2.2. Natural Adsorbent and Immobilizer Collection and Characterization

A river sediment (RS), consisting of silty sand, was used as a natural adsorbent or immobilizer in this study because a river is located near the tunnel excavation site.

After collecting the RS using hand shovels, the sample was air-dried in the laboratory and sieved to be less than 2 mm. The RS is finely grained sand, composed of 58.4% of sand, 30.7% of silt and 10.9% of clay. XRF and XRD were also used to determine the chemical and mineralogical compositions of the adsorbent, respectively. The amorphous Al and Fe phases in the adsorbent was determined using acidic oxalate solution extraction because these phases have significant effects on As adsorption [50–52].

2.3. Batch Adsorption Experiments

Batch adsorption experiments were carried out by mixing predetermined amounts of the RS and As(V) solution of specified concentrations at 120 rpm using a reciprocal shaker. After 24 h, the suspensions were filtered through 0.45 µm Millex® membrane filters (MerckMillipore, Burlington, MA, USA) and then the filtrates were analyzed. The As(V) solutions used in these experiments were prepared by dissolving reagent grade $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ powder in deionized water (18 MΩ cm). In all of these preparations, the deionized water used was obtained from a Millipore Milli-Rx 12α system (Merck Millipore, Burlington, MA, USA). The concentration of As retained in the RS was calculated using the following Equation (1):

$$q = \frac{(C_0 - C) \cdot V}{W} \quad (1)$$

where, q is adsorbed amount (mg/g), C_0 is initial As concentration (mg/dm³), C is final As concentration (mg/dm³), V is volume of solution (dm³), and W is weight of RS (g).

Data from the experiments were fitted with non-linear Langmuir isotherm. Under equilibrium conditions, adsorption of As can be represented by the following reaction (2) [53]:

$$q = \frac{q_{\max} \cdot K_L \cdot C}{1 + K_L \cdot C} \quad (2)$$

where, $q_{\max}$ (mg/g) is the maximum adsorption capacity and K_L is the adsorption equilibrium constant.

2.4. Laboratory and In Situ Column Experiments

Two types of column experiments were conducted in the laboratory and in situ to evaluate the effects of column conditions, such as quality, intensity and frequency of rainwater and temperature on As leaching from the excavated rocks and adsorption and immobilization of the RS. The column with the inner diameter of 5.2 cm and height of 35.0 cm was used in the laboratory whereas the column with the inner diameter of 10.4 cm and height of 35.0 cm was used in situ. The larger diameter of the columns was used in the in situ conditions to collect natural rainfall more effectively. The schematics of the two columns are illustrated in Figure 1. Crushed mudstone and the RS were packed in eight columns, four in the laboratory and four in situ. The details of experimental conditions are summarized in Table 1, the columns are referred to by the following notations:

- L-T1: crushed T1 sample only in laboratory column,
- L-T1-AL: crushed T1 sample with bottom adsorption layer in laboratory column,
- I-T1: crushed T1 sample only in situ column,
- I-T1-AL: crushed T1 sample with bottom adsorption layer in situ column,
- L-T2: crushed T2 sample only in laboratory column,
- L-T2-Im: crushed T2 sample mixed with RS as immobilizer in laboratory column,
- I-T2: crushed T2 sample only in situ column,

- I-T2-Im: crushed T2 sample mixed with RS as immobilizer in situ column.

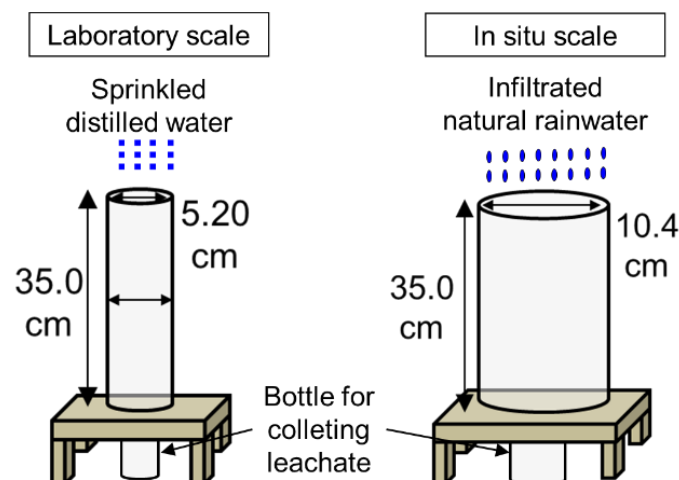


Figure 1. Schematic diagrams of laboratory and in situ column experiments.

Meanwhile, RS was used as the material of the adsorption layer for the T1 sample, and mixed with the T2 sample to immobilize As. The differences in the layers of columns are due to the different As leaching concentrations; that is, the As leaching concentration from T2 sample ($>0.3 \text{ mg/dm}^3$) was higher than that from T1 sample. The thickness of the adsorption layer was set at 4 cm based on the previous research to prevent forming of water-flow channels in the adsorption layer and to uniformly percolate in the adsorption layer. The mixing ratio of the T2 sample to the RS was set at 30% by weight based on the previous results that As leaching concentration was reduced to be less 0.3 mg/dm^3 . Distilled water (0.05 dm^3) was sprinkled each week on top of the column in the laboratory. The amount of water sprinkled corresponded to a weekly precipitation of 23.5 mm observed by the meteorological institute located near the tunnel construction site. The effluent was collected using 0.1 dm^3 bottles set under the column after 2 days. For the in situ columns, natural rainwater infiltrated from the top of the column. The effluent from the column was collected using 0.5 dm^3 bottles set under the column every month.

The pH and Eh of effluents were measured and then filtered through $0.45 \mu\text{m}$ membrane filters for chemical analysis. The periods of experiments in the laboratory and in situ were 26 weeks and 30 weeks, respectively.

To evaluate the differences in cumulative leached As from the rock sample, cumulative leachability, CL/M (mg/kg), was calculated using the following Equation (3):

$$\frac{CL}{M} = \sum_i^n \frac{C_i \times V_i}{M_i} \quad (3)$$

where, C_i (mg/dm^3) is leaching concentration of As in the leachate, V_i (dm^3) is the volume of leachate collected in each sampling, M_i (kg) is the mass of packed rock sample in the column, and n the number of collected leachate.

2.5. Chemical Analysis

Concentrations of As in leachates were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS) (iCAP Qc, Thermo Fisher Scientific, Waltham, MA, USA) (margin of error = $\pm 5\%$). The major ions in the leachate were determined by ion chromatographs (ICS-90 and ICS-2000, Dionex Corporation, Sunnyvale, CA, USA) (margin of error = $\pm 2\%$) or inductively coupled plasma atomic emission spectrometer (ICP-AES) ICP-AES (ICPE-9800, Shimadzu Corporation, Japan) (margin of error = $\pm 2\%$).

Table 1. List of laboratory and in situ column experimental conditions.

Case			L-T1	L-T1-AL	I-T1	I-T1-AL	L-T2	L-T2-Im	I-T2	I-T2-Im
Condition			Laboratory		IN Situ		Laboratory		In Situ	
Used Rock Sample			T1 Sample				T2 Sample			
Usage of RS			–	AL *	–	AL *	–	Im **	–	Im **
Rock layer	Thickness	cm	20.0	20.0	20.0	20.0	20.0	–	20.0	–
	Weight	g	620	620	2288	2288	663	–	2540	–
	Soil density	g/cm ³	2.71	2.71	2.71	2.71	2.76	–	2.76	–
	Column density	g/cm ³	1.46	1.46	1.35	1.35	1.56	–	1.50	–
	Porosity	%	46.1	46.1	50.2	50.2	43.4	–	45.8	–
	Pore volume	cm ³	196	196	853	853	184	–	778	–
Adsorption layer	Thickness	cm	–	4.00	–	4.00	–	–	–	–
	Weight	g	–	103	–	428	–	–	–	–
	Soil density	g/cm ³	–	2.70	–	2.70	–	–	–	–
	Column density	g/cm ³	–	1.21	–	1.26	–	–	–	–
	Porosity	%	–	55.2	–	53.3	–	–	–	–
	Pore volume	cm ³	–	46.8	–	181	–	–	–	–
Total	Thickness	cm	–	24.0	–	24.0	20.0	20.0	20.0	26.0
	Weight	g	–	723	–	2716	663	638 (T2: 447 g, RS: 191 g)	2540	3630 (T2: 2540 g, RS: 1090 g)
	Soil density	g/cm ³	–	–	–	–	2.76	2.74	2.76	2.74
	Column density	g/cm ³	–	–	–	–	1.56	1.50	1.50	1.64
	Porosity	%	–	47.6	–	50.7	43.4	45.1	45.8	40.0
	Pore volume	cm ³	–	242	–	1034	184	192	778	883

*: Bottom adsorption layer. **: Mixing rock sample with RS as immobilizer.

3. Results and Discussion

3.1. Chemical and Mineralogical Properties of Rock Samples and River Sediment

The two rock samples are predominantly composed of silicate and alumino-silicate minerals like quartz (SiO₂) and albite (NaAlSi₃O₈), and contain kaolinite (Al₄Si₄O₁₀(OH)₈) in minor amounts. In addition, the T2 sample also contains muscovite (KAl₂[(OH)₂/AlSi₃O₁₀]) in minor amounts (Tables 2 and 3). Although XRD could not detect trace minerals, the T1 sample contains trace amounts of pyrite, which was detected by the microscopic observation. The arsenic content of samples T1 and T2 were 6.8 and 20.5 mg/kg, respectively, which is within or higher than the reported average As content of sedimentary rocks (5–10 mg/kg) [54,55].

Table 2. Chemical composition of excavated rock and RS (river sediment) samples.

Sample		T1	T2	RS
SiO ₂	wt. %	68.2	64.3	62.0
TiO ₂	wt. %	0.7	0.6	1.0
Al ₂ O ₃	wt. %	16.5	18.8	20.9
Fe ₂ O ₃	wt. %	6.3	5.3	7.7
MnO	wt. %	<0.1	0.1	0.1
MgO	wt. %	2.6	2.3	2.9
CaO	wt. %	0.9	2.4	1.8
Na ₂ O	wt. %	<0.1	3.0	<0.1
K ₂ O	wt. %	2.9	2.7	1.9
P ₂ O ₅	wt. %	1.6	<0.1	1.5
SO ₃	wt. %	0.2	0.4	<0.1
Total	wt. %	99.9	99.9	99.8
As	mg/kg	6.8	20.5	11.2
LOI	wt. %	4.8	7.2	4.4
TOC	wt. %	0.22	0.20	0.20
IC	wt. %	0.11	0.52	<0.01
Amorphous Al	mg/g	0.6	2.3	1.4
Amorphous Fe	mg/g	13.4	4.8	3.9

Table 3. Mineral composition of used rock and RS samples.

Sample	T1	T2	RS
Quartz	+++	+++	+++
Albite	++	++	++
Siderite		+	
Muscovite	+		+
Kaolinite	+	+	+

Intensity of X-ray peak: +++:strong, ++:medium, +:weak.

The RS sample is predominantly composed of silicate and alumino-silicate minerals like quartz and albite, and contains minor amount of clay minerals, such as a kaolinite (Tables 2 and 3). Although the As content of the RS was 11.2 mg/kg, which is slightly higher than that of T1 sample, As leaching concentration from the RS by batch experiments was below the Japanese environmental standard (0.01 mg/dm³).

Amorphous Al and Fe contents in the RS were 1.4 and 3.9 mg/g, respectively, which are relatively lower compared to iron-rich natural adsorbents (10 to 100 mg/g), which are obtained in southwest region of Hokkaido [48]. Since the RS contains kaolinite, it would be effective in As adsorption [56].

3.2. Batch Adsorption Experiments

Figure 2 shows the Langmuir isotherm of As(V) for the RS. As(V) adsorption onto the RS fitted well with the Langmuir isotherm (coefficient of correlation = 0.99). The q_{max} and K_L of the Langmuir isotherm had values of 0.099 mg/g and 1.88 dm³/g, respectively. The pH during the As(V) adsorption experiments was weakly alkaline to neutral ranging from 5.9 to 6.8. These results indicated that although q_{max} of RS was lower than that of natural adsorbents, e.g., natural/modified clay [57] and natural laterite [58], the RS had

a significant adsorption capacity for As(V) due to the contained Fe oxide, amorphous Fe, and clay minerals such as a kaolinite [50,51,56].

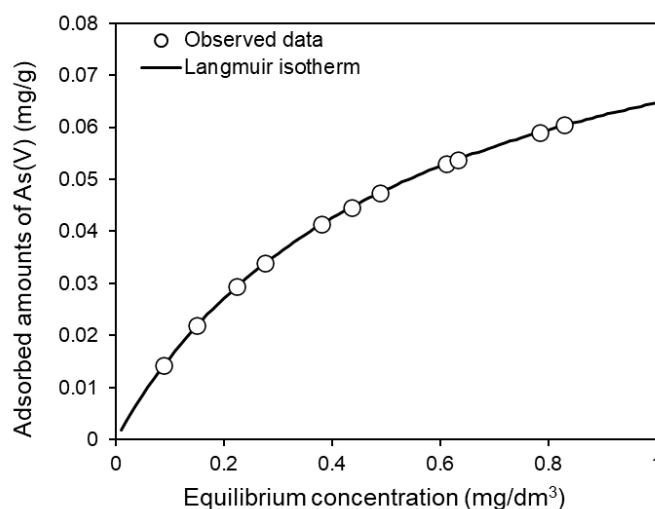


Figure 2. Adsorption characteristic of As onto RS fitted with Langmuir isotherm of As(V) for RS.

3.3. Column Experiments

3.3.1. Changes in Arsenic

Figure 3 shows the changes in As concentration in the leachate for laboratory and in situ column experiments using samples T1 and T2. The x axis is the pore volume (PV), which can be calculated using the cumulative leachate volume divided by pore volume of the rock layer, mixing layer, or rock layer with adsorption layer. The y axis is the measured concentration in the leachate.

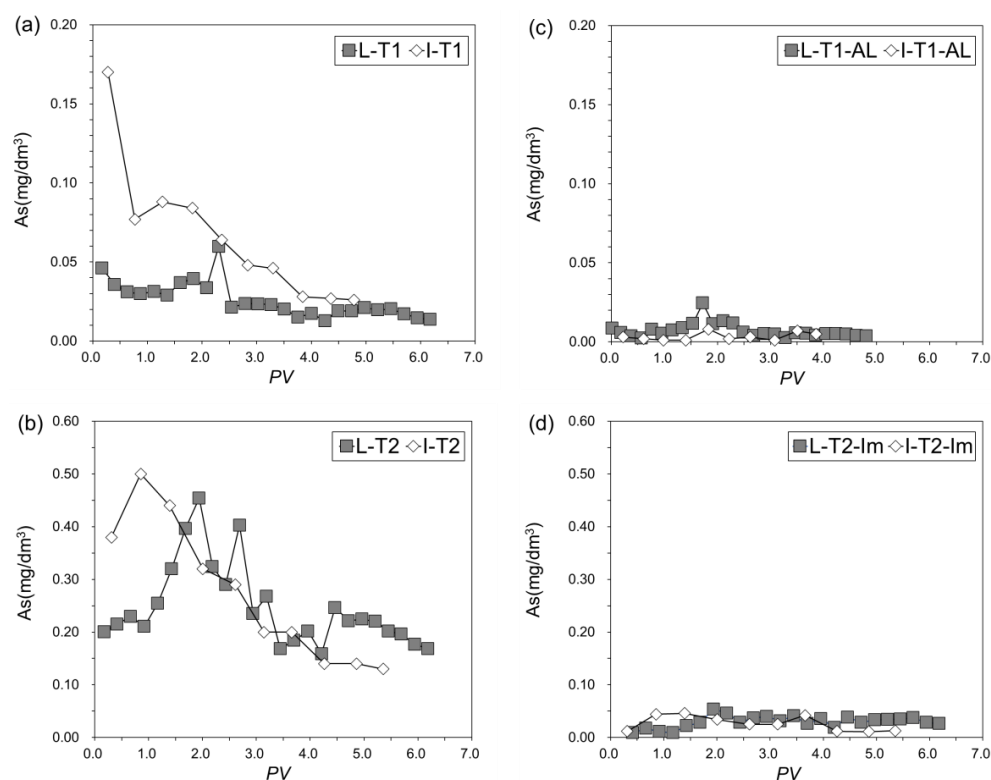


Figure 3. Changes in As concentrations with PV; (a) comparison between L-T1 and I-T1, (b) comparison of L-T2 and I-T2, (c) comparison between L-T1-AL and I-T1-AL and (d) comparison between L-T2-Im and I-T2-Im.

In laboratory column experiments consisting of only rock samples, in cases of L-T1 and L-T2, the peak As concentrations of 0.06 and 0.46 mg/dm³, respectively, were observed at around $PV = 2.0$, and then gradually decreased to about 0.02 and 0.20 mg/dm³, respectively. In comparison, in situ column experiments showed the peak As concentrations of 0.17 and 0.50 mg/dm³ in cases of I-T1 and I-T2, respectively, at less than or around $PV = 1$, which dramatically decreased to about 0.03 and 0.15 mg/dm³, respectively. In other words, the peak concentration was observed at $PV = 2.0$ in the laboratory while in situ, the peak was observed at the beginning of experiment.

In the laboratory column experiments with RS, consisting of the rock samples and RS, L-T1-AL and L-T2-Im, As leaching concentrations were reduced, and the presences of the As peak was retarded by the bottom adsorption layer for the T1 sample or by mixing of the RS with the T2 sample. For in situ column experiments, I-T1-AL and I-T2-Im, the same trends were observed, resulting in the reduction and retardation of As leaching from both rock samples.

These results imply that at the beginning of the column experiments consisting of only rock samples, dried rock samples reacted with infiltrated water, and high As leaching from rock samples were released until around $PV = 1.0$ to 3.0 [59]. After the water content in the column became constant, low and steady, As concentrations were observed due to pseudo-steady state leaching and adsorption.

3.3.2. Cumulative Leachability of As

Figure 4 shows the CL/M of As with time. The CL/M of As in all cases continuously increased until the end of the experiment. The CL/M of As in cases of L-T1 and I-T1 were 0.050 and 0.13 mg/kg at $PV = 5.0$, respectively, and those in cases of L-T2 and I-T2 were 0.38 and 0.45 mg/kg at $PV = 5.0$, respectively. By setting the bottom RS layer or mixing of the RS with the rock sample, the CL/M of As dramatically decreased and was lower than 0.010 mg/kg in $PV = 5.0$ in cases of L-T1-AL and I-T1-AL, and 0.050 mg/kg in $PV = 5.0$ in cases of L-T2-Im and I-T2-Im, respectively.

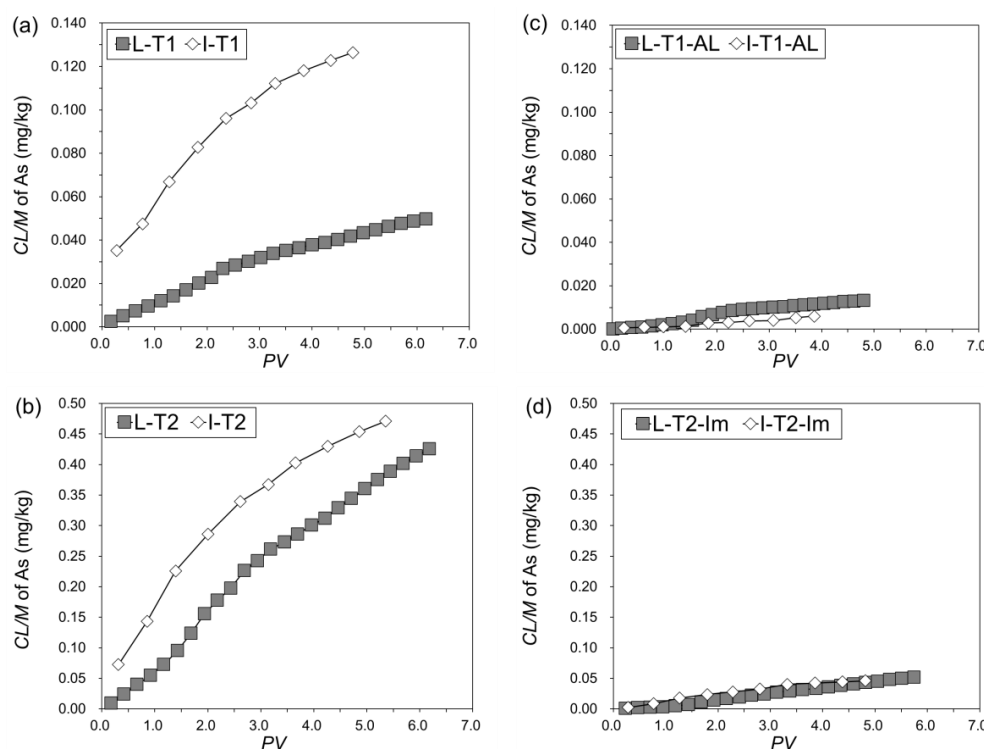


Figure 4. Changes in CL/M of As with PV; (a) comparison between L-T1 and I-T1, (b) comparison between L-T2 and I-T2, (c) comparison between L-T1-AL and I-T1-AL and (d) comparison between L-T2-Im and I-T2-Im.

These results showed that the CL/M of the in situ column experiments was higher than those of the laboratory column experiments only in the case of the rock sample. In comparison, when the RS was set as an adsorption layer or mixed with the rock layer, a dramatic reduction was observed for both the laboratory and in situ column experiments. Thus, although in situ condition affected As leaching from rock layer, it would not significantly affect adsorption or immobilization by the RS.

By using the results of the CL/M of As and weight of the rock layer for each column, the amounts of As leaching of L-T1, I-T1, L-T2 and I-T2 were calculated: 0.078, 0.11, 0.31 and 1.1 mg, respectively. The amounts of adsorbed of the RS for L-T1-AL, I-T1-AL, L-T2-Im and I-T2-Im also were evaluated at 0.19, 0.77, 0.34 and 1.9 mg, respectively, by assuming that the equilibrium concentration of As was equal to 0.01 mg/dm^3 . The above results indicate that the RS still has enough adsorption capacity for As leached from the rock layer.

3.3.3. Changes of pH, Eh, and SO_4^{2-}

Adsorption is strongly influenced by pH and Eh [60,61]. So, the changes of pH and Eh for laboratory and in situ column experiments are shown in Figures 5 and 6. In addition, the dissolution of sulfide minerals is a crucial factor for As leaching from rock samples [62]. Thus, concentrations of major coexisting sulfate ion (SO_4^{2-}) in the leachate for laboratory and in situ column experiments are shown in Figure 7. The pH values in eight columns ranged from 7.5 to 9.0, which were slightly alkaline. The pH changes in eight cases exhibited almost the same pattern. However, pH changes under in situ conditions, such as in cases of I-T1, I-T2 and I-T2-Im, were slightly lower compared to those of the laboratory conditions. The Eh values in eight columns ranged from +330 to +480 mV, which means that the redox conditions were oxidic. The Eh values under in situ conditions were also relatively higher than those under laboratory conditions.

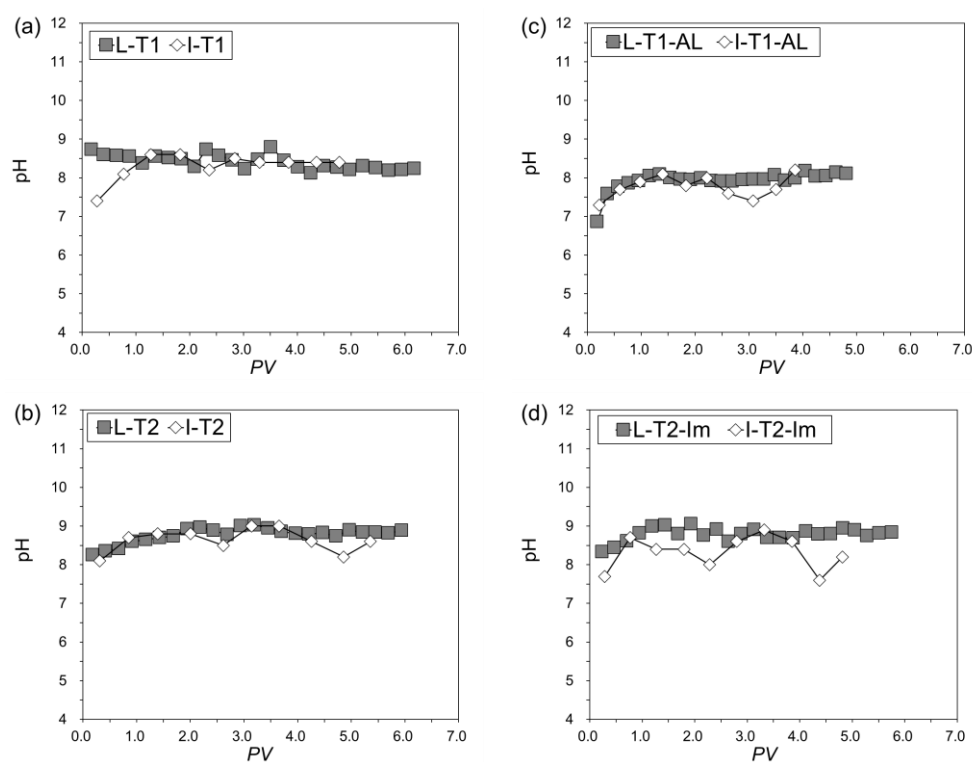


Figure 5. Changes in pH with PV; (a) comparison between L-T1 and I-T1, (b) comparison between L-T2 and I-T2, (c) comparison between L-T1-AL and I-T1-AL and (d) comparison between L-T2-Im and I-T2-Im.

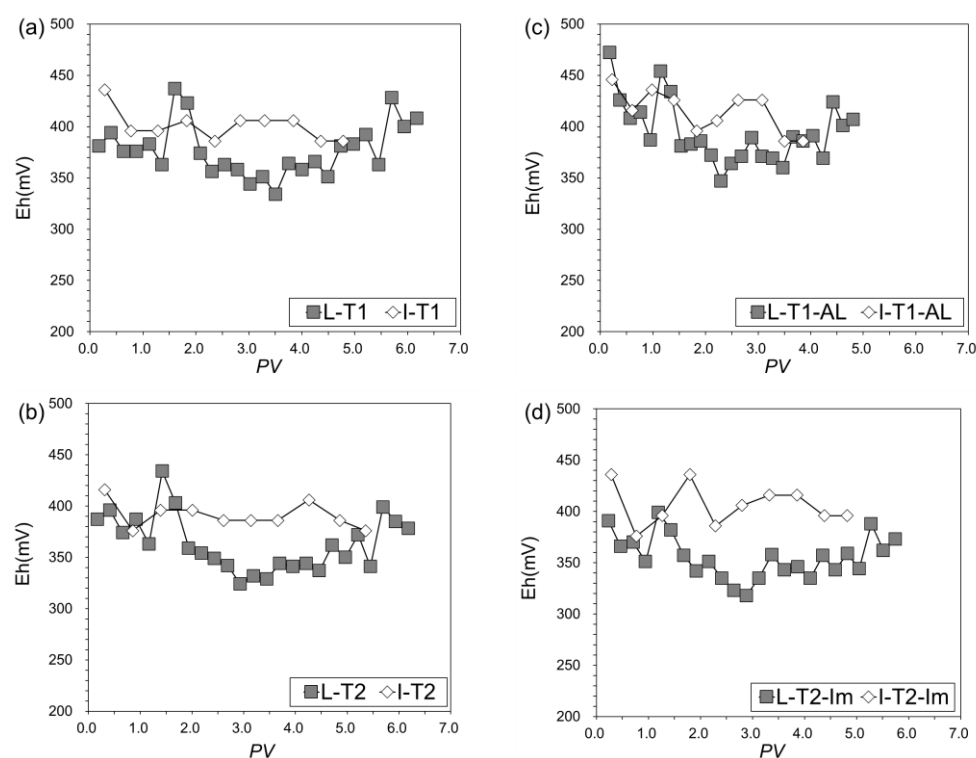


Figure 6. Changes in Eh with PV; (a) comparison between L-T1 and I-T1, (b) comparison between L-T2 and I-T2, (c) comparison between L-T1-AL and I-T1-AL and (d) comparison between L-T2-Im and I-T2-Im.

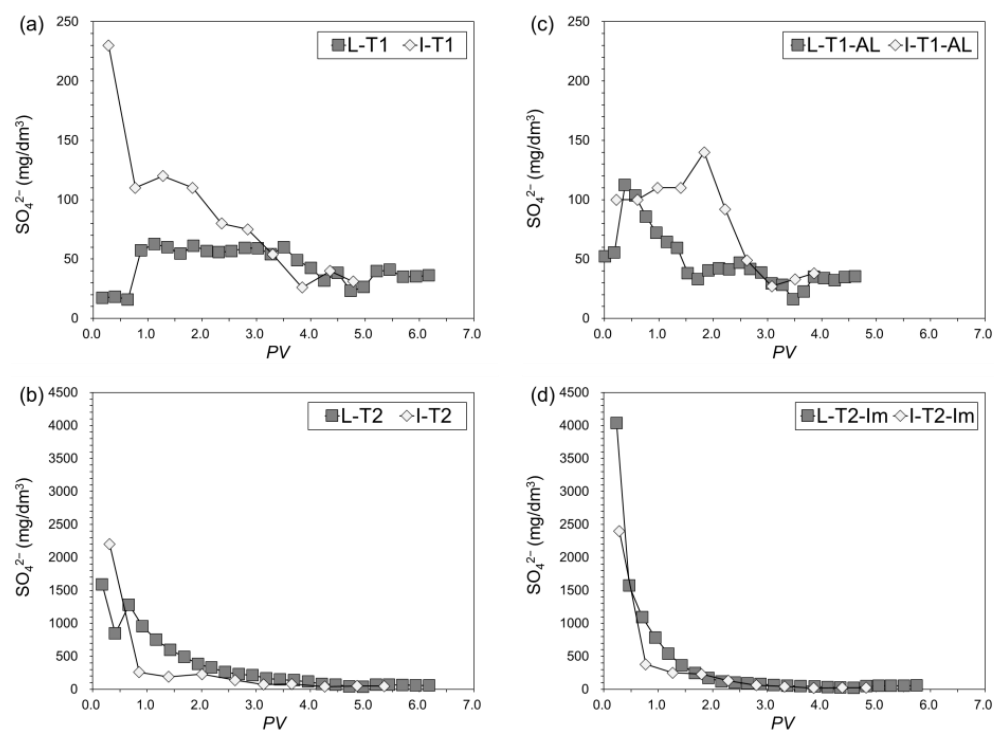


Figure 7. Changes in SO_4^{2-} concentrations with PV; (a) comparison between L-T1 and I-T1, (b) comparison between L-T2 and I-T2, (c) comparison between L-T1-AL and I-T1-AL and (d) comparison between L-T2-Im and I-T2-Im.

The peak leaching concentrations of SO_4^{2-} , except in cases of L-T1-AL and I-T1-AL, were observed in the beginning, and then the concentrations of SO_4^{2-} dramatically de-

creased. This means that sulfide minerals such as pyrite are dissolved at the beginning of column experiments. By comparing laboratory and in situ conditions for columns consisting of only rock layer, SO_4^{2-} leaching concentrations in the in situ condition were relatively higher than those of the laboratory condition.

These results indicate that in situ columns are exposed to more oxic conditions compared to the laboratory columns, which would induce oxidation and dissolution of sulfide minerals contained in rock samples, resulting in slight decreases of pH and increases of Eh in the leachate. [63,64].

3.3.4. Recovery Ratio

To evaluate the effects of evaporation and residual pore water, the recovery ratio of collected leachate volume to sprinkled distilled water volume for the laboratory columns and that to rainfall observed in the nearest meteorological station for the in situ columns were calculated. Figure 8 shows the ratios for laboratory and in situ column experiments. For the laboratory columns, the initial recovery ratios of L-T1, L-T2, L-T1-AL and L-T2-Im were 0.63, 0.61, 0.05, and 0.90, respectively, due to packing the rock dried in room temperature in the column. After the second collection, the ratios of all four cases approached approximately 0.90. This means that approximately 10% of sprinkled distilled water was evaporated during the experiment. Under in situ conditions, the initial recovery ratios of I-T1, I-T2, I-T1-AL and I-T2-Im were 0.20, 0.21, 0.19, and 0.21, respectively. However, after the rock sample in the column became wet, the ratios of four cases fluctuated between 0.50 and 1.25. This is due to the frequency and intensity of rain, changes in temperature, humidity, and solar radiation. These factors may affect unstable recovery of the leachate, i.e., unsteady-state infiltration for in situ column experiments.

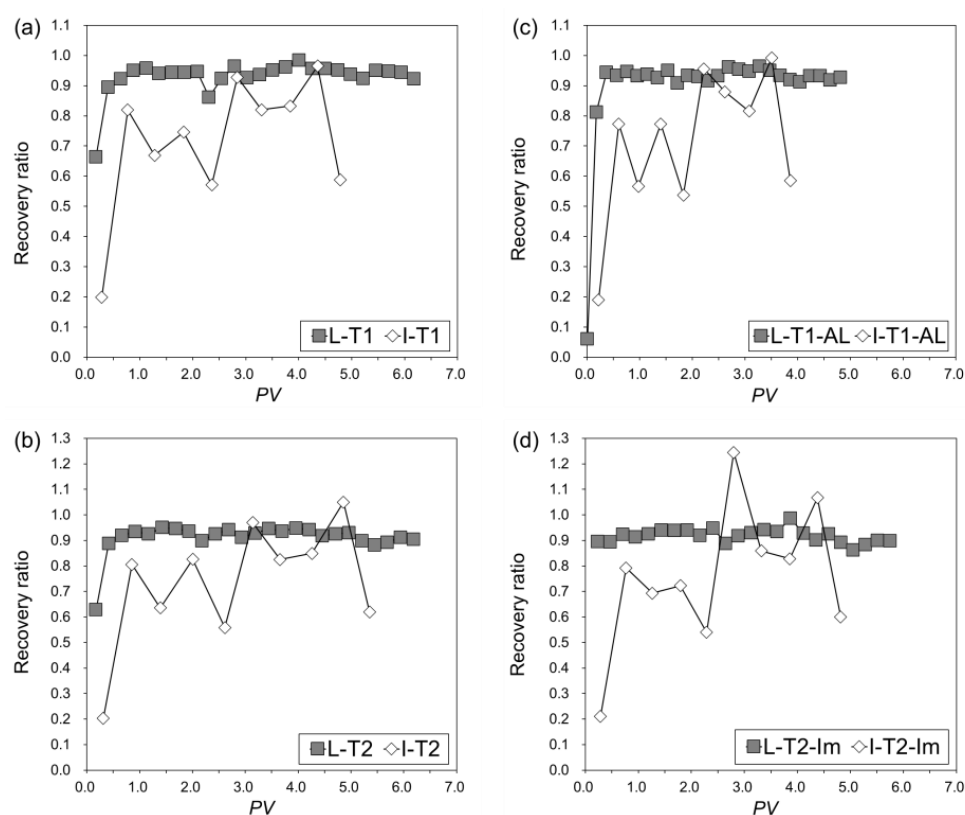


Figure 8. Changes in recovery ratio with PV; (a) comparison between L-T1 and I-T1, (b) comparison between L-T2 and I-T2, (c) comparison between L-T1-AL and I-T1-AL and (d) comparison between L-T2-Im and I-T2-Im.

The above results indicate that the water content of the in situ columns is likely to be lower because the recovery ratios in the in situ columns were lower and fluctuated. These results are consistent with the results of the evolution of Eh and SO_4^{2-} in the leachate [43,44].

3.3.5. Temperature and Rainfall under In Situ Conditions

Figure 9 illustrates the changes in rainfall and temperature of the in situ columns. The x axis shows the experimental period. The left y axis shows As leaching concentrations in the leachate in cases of I-T1 and I-T2, and the right y axis shows rainfall and temperature observed in the meteorological station nearest to the in situ columns.

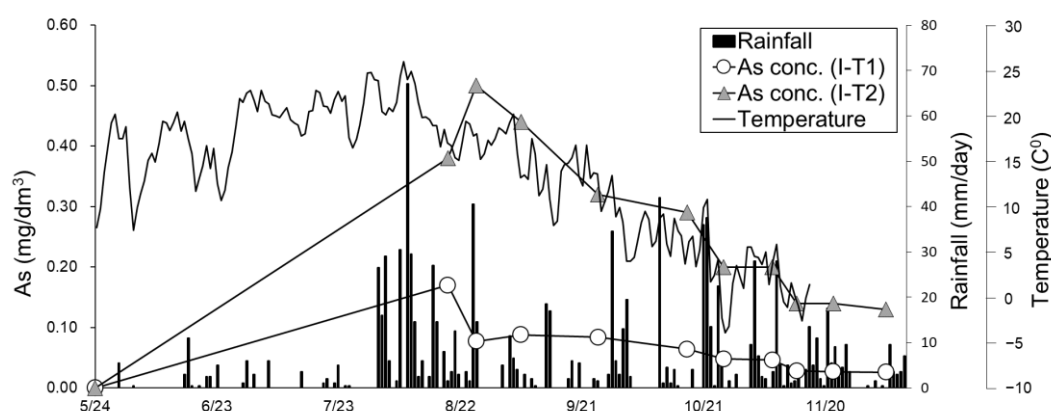


Figure 9. Changes in As concentration, precipitation and temperature under in situ conditions in cases of I-T1 and I-T2.

In cases of I-T1 and I-T2, As leaching concentrations of the first and second collected leachates were relatively high, and then gradual decreases were observed. This is due to the relatively high temperatures in the summer month (May to August) and the heavy rainfall from July to August until the recovery of the first and second leachates.

This means that not only were there lower water contents in the in situ columns but also a higher temperature, which induced the oxidation of sulfide minerals in the columns.

3.3.6. Significance of Environmental Conditions for As Behavior

By comparing the results of column experiments conducted in the laboratory and in situ, As leaching concentrations were higher, the pH values were slightly lower, the Eh values were higher, and the SO_4^{2-} concentrations were higher under in situ conditions. In addition, since the in situ column experiments were conducted in summer to autumn, the temperature was relatively high and heavy rainfall events were observed. Meanwhile, almost constant water content and constant room temperature were established for the laboratory columns.

Based on the comparison between the laboratory columns and the in situ columns, the oxidation of sulfide minerals in the rock samples, or weathering of the rock, is accelerated by the effects of higher temperature and lower water contents due to rainfall conditions. Figure 10 illustrates the relationship between As and SO_4^{2-} leaching concentrations in the leachate in cases of L-T1, I-T1, L-T2 and I-T2. Positive correlations were observed between As and SO_4^{2-} in I-T1 and I-T2. Thus, in situ conditions enhanced dissolution of SO_4^{2-} , and As leaching was accelerated [65,66]. Therefore, it is important to conduct long-term column experiments by considering in situ conditions, including weather conditions, when evaluating As leaching behavior from mudstone excavated rocks. Our previous studies also noted the complex nature of As leaching and immobilization in in situ embankment and column experiments, respectively [20,46].

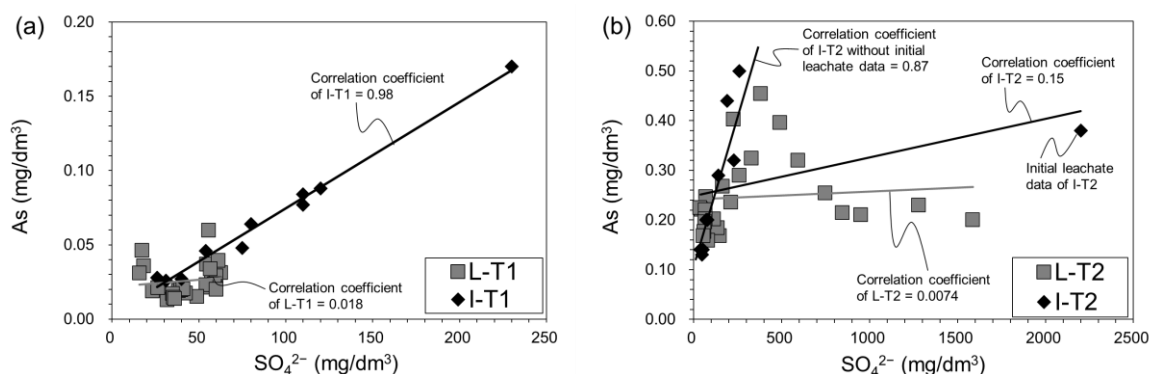


Figure 10. Correlation between As and SO_4^{2-} concentrations; (a) comparison between L-T1 and I-T1 and (b) comparison between L-T2 and I-T2. Correlation coefficients of L-T1, I-T1, L-T2 and I-T2 are equal to 0.018, 0.98, 0.0074 and 0.15, respectively, whereas that of I-T2 without initial leachate data is 0.87.

When the natural adsorbent was used as an additive of adsorption layer or immobilizer, no significant differences in reducing As leaching concentration between laboratory and in situ columns were observed. The adsorbent used in this study contained amorphous Al/Fe and Al/Fe oxides that are effective in As adsorption or immobilization under acidic to weak alkaline pH ranges. However, when pH increased higher than 9.5, adsorption by amorphous Al/Fe and Al/Fe oxides is dramatically restricted [50–53,67]. Since the leachate pH under in situ conditions in this study fluctuated from a neutral to a weak alkaline pH, ranging from 7 to 9, pH did not affect As adsorption or immobilization by the RS. This indicates that although the adsorption of As by the RS is strongly influenced by leachate pH, the adsorption properties did not depend on the pH due to the narrow pH range.

To reduce the leaching of As from excavated rocks, the effect of oxidation should be restricted. Covering soil is often used for the embankment of excavated rocks in order to minimize gaseous oxygen and water intrusion into rock layer [68]. Thus, when the evaporation from the surface and oxidation of rock layer are mitigated, laboratory columns are effective in evaluating the leaching and adsorption behaviors of As. Therefore, it is important to distinguish the column conditions when evaluating the fate of As from excavated rocks.

4. Conclusions

This study compared the results of laboratory and in situ column experiments using tunnel excavated rocks containing significant amounts of As and the RS as a natural adsorbent and immobilizer for reducing As leaching concentration to evaluate the effects of column conditions, such as temperature, intensity and frequency of rainwater. The findings of this study are summarized as follows:

1. Arsenic leaching concentration from rock samples conducted in situ were slightly higher than those conducted in the laboratory. However, the significant adsorption of As by the RS was observed in both the laboratory and in situ column experiments.
2. The pH of in situ column was slightly lower compared to the laboratory columns, whereas Eh and SO_4^{2-} leaching concentration of the in situ columns were slightly higher compared to those in the laboratory.
3. The lower water content and higher temperature of in situ columns enhanced the oxidation of sulfide minerals in the rock, which induced higher leaching of As.
4. Although adsorption of As by the RS was influenced by pH in the leachate, the difference of the leachate pH released from the sedimentary rock samples used in this study between laboratory and in situ column experiments was insignificant due to their nearly equivalent pH.

The above results suggest that when evaluating As leaching concentration from excavated rock samples, environmental conditions are important and in situ conditions

are preferable. However, laboratory column experiments can be used as alternative when certain conditions are satisfied (e.g., uniform water content within the columns).

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