

## Effects of adsorption and covering-soil layers on arsenic leaching from excavated rocks

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### Abstract

Leachate containing arsenic (As) was observed from excavated rocks of tunnels located in the north of Hokkaido, Japan. The leachate could potentially contaminate the surrounding soil and groundwater environment. Thus, column leaching experiments using the excavated rocks with adsorption and covering-soil layers both consisting of a river sediment were carried out to identify the leaching mechanism of As and to decrease the leaching concentration of As from the rocks. The leachate from the column packed only with the excavated rocks showed alkaline pH and As concentration exceeding the environmental standard of Japan. The As concentration was correlated with iron and sulfate concentrations in the leachate. This indicates that the As leaching results from oxidation of pyrite contained in the rocks. The column having an adsorption layer showed that the adsorption layer reduced pH of the leachate near neutral and that the leaching concentration of As decreased. In particular, As concentration dramatically decreased to approximately 2 µg/L when the column had both adsorption and covering-soil layers. This means that both layers can reduce oxygen concentration in the rock layer, which reduce the rate of oxidation and the leaching of As.

**Keywords:** Arsenic, column experiments, pyrite, adsorption, covering-soil layer

## 1. Introduction

Arsenic (As) is well known as one of toxic elements, which affects human health. It has been reported that hydrothermally altered rocks and mudstone of marine origin have potential hazard because they release a variety of toxic elements such as As (Tabelin and Igarashi, 2009; Tabelin et al., 2010; Tabelin et al., 2013). When such rocks are disposed, the hazardous elements may be leached out and contaminate surrounding environment and groundwater. To solve this issue, these rocks have been covered with sealing sheet or geomembrane to isolate the rocks from rainwater and groundwater. However, this method is expensive and impractical due to a huge volume of excavated rocks produced in a short term. Thus, reasonable methods to dispose the rocks are required.

Recently, the adsorption layer method has been reported as one of the reasonable countermeasures (Tabelin et al., 2013; Tatsuhara et al., 2012). Therefore, column experiments with an adsorption

layer were conducted. In addition, a column experiment with both adsorption and covering-soil layers were carried out to understand effects of these layers on As leaching.

## 2. Materials and Methods

### 2.1 Sample collection

An excavated rock sample used in this study was collected from a tunnel (OT tunnel) located in the north of Hokkaido, Japan. The rock sample was collected from a storage site of As-rich excavated rocks. The sample was brought back to the laboratory, and crushed by a jaw crusher, air dried in room temperature, and sieved through a 20 mm aperture screen. The <20 mm fraction was used for the experiments.

A river sediment used in this study was taken from a river near the tunnel construction site by using a shovel at random points of the impoundment, and air dried at room temperature, lightly crushed using mortar and pestle, and sieved through a 2 mm

aperture screen. The <2 mm fraction was used as adsorption and covering-soil layers in the experiments.

## 2.2 Chemical and mineralogical analyses of the samples

To measure the chemical and mineralogical properties of the rock sample and river sediment, an X-ray fluorescence spectrometer (XRF) and X-ray diffractometer (XRD) were utilized. In the preparation for the analyses, the excavated rocks and river sediment were crushed to <50  $\mu\text{m}$ . Spectro Xepos (Rigaku corporation, Japan) and Multi Flex (Rigaku corporation, Japan) were used for chemical and mineralogical analyses, respectively. In addition, a scanning electron microscope (SEM: Shimadzu Corporation, Japan) and energy dispersive X-ray spectrometry (EDX: Shimadzu Corporation, Japan) were used to identify trace minerals in excavated rocks. In this analysis, the excavated rocks of the other tunnel located in the same geological formation near OT tunnel were used because the fresh excavated rocks of OT tunnel could not be collected.

## 2.3 Column experiments

The details of columns used are depicted in Fig. 1. In the experiments, five columns were constructed to understand the leaching and adsorption behaviors by the effects of an infiltration rate and covering-soil layer. Cases 1-1 and 1-2 had only excavated rock layer. Cases 2-1 and 2-2 had excavated rock and

adsorption layers. Case 3 had both covering-soil and adsorption layers on and under the excavated rocks. Distilled water was poured at 50 mL/week in Cases 1-1 and 2-1, and 200 mL/week in Cases 1-2, 2-2, and 3. Each layer was separated by a PVC net and No. 5C filter.

After collecting the effluent, temperature, pH, oxidation reduction potential (ORP), and electrical conductivity (EC) were measured. The effluent samples were filtrated through 0.45  $\mu\text{m}$  Millex® filters and provided for chemical analysis.

## 2.4 Chemical analysis of effluent

Concentration of dissolved As higher than 0.1 mg/L was analyzed by using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan). Concentration of dissolved As less than 0.1 mg/L was analyzed by using the ICP-AES connected with a hydride vapor generator. Before analyzing As, effluent samples were filtrated through Sep-pak® cartridge (Waters Corporation, USA) to remove As(V). Thus, total As and As(III) were analyzed directly by using ICP-AES. As(V) concentration was calculated by the following equation.

$$\text{As(V)} = \text{Total As} - \text{As(III)}$$

Concentrations of coexisting ions were determined by using cation and anion chromatographs (ICS-90 and ICS-1000, Dionex Corporation, USA).

## 3. Results

### 3.1 Properties of samples

Mineralogical and chemical compositions of the excavated rock and river sediment were listed in Tables 1 and 2, respectively. The excavated rock

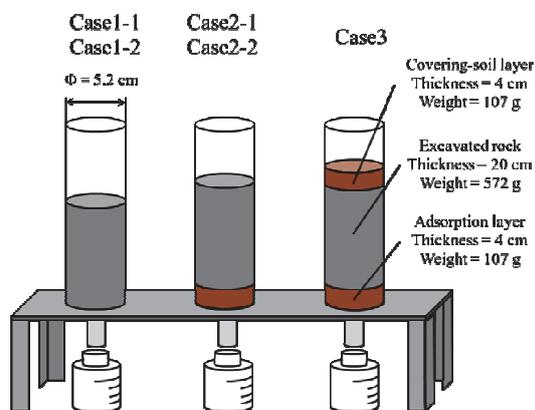


Fig. 1 Schematic diagram of columns used in the experiments

Table 1 Mineralogical properties of the rock and river sediment

Minerals	Quartz	Albite	Siderite
OT	+++	++	+
River sediment	+++	++	

+++ : Strong, ++ : Medium, + : Weak

Table 2 Chemical composition of the rock and river sediment

Sample	SiO <sub>2</sub> (wt.%)	TiO <sub>2</sub> (wt.%)	Al <sub>2</sub> O <sub>3</sub> (wt.%)	Fe <sub>2</sub> O <sub>3</sub> (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na <sub>2</sub> O (wt.%)	K <sub>2</sub> O (wt.%)	P <sub>2</sub> O <sub>5</sub> (wt.%)	SO <sub>3</sub> (wt.%)	As (mg/kg)
OT	61.3	0.59	12.3	5.94	0.05	1.87	1.13	1.80	2.92	0.06	0.17	6.3
River sediment	55.3	0.81	15.2	6.97	0.16	2.02	1.75	1.35	1.73	0.07	-	0.9

- : Under the detection limit

contains 6.3 mg/kg of As whereas the river sediment contains As less than 1 mg/kg.

Figure 2 shows the SEM image of sulfur and iron in the excavated rock of the other tunnel located in the same geological formation near OT tunnel. Trace pyrite was observed in this figure. The results of the chemical analysis of the point showed 55wt.% of Fe and 45wt.% of S. This means that the excavated rock of OT tunnel contains pyrite. Since pyrite in hydrothermally altered rocks contains As (Tabelin et al., 2012), As is likely to be contained in the rock.

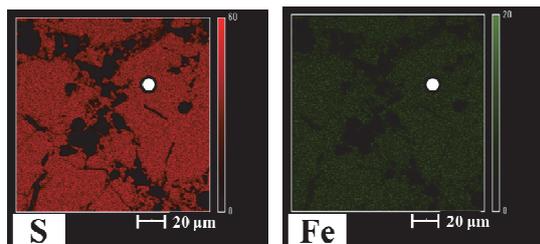


Fig. 2 SEM image of the rock

### 3.2 As concentration of effluent from columns

Figure 3 shows total As concentration of effluent from the columns in Cases 1-1 and 1-2 at an irrigation rate of 50 mL/week. Except the As concentration at the 4<sup>th</sup> week, total As concentration in Case 2-1 was less than that in Case 1-1. Furthermore, total As concentration in Case 2-1 was less than As environmental standard in Japan (10 μg/L) except at 4<sup>th</sup> and 5<sup>th</sup> weeks whereas that in Case 1-1 exceeded the standard for all weeks. The highest total As concentrations in Cases 1-1 and 2-1 were 50 and 36 μg/L, respectively.

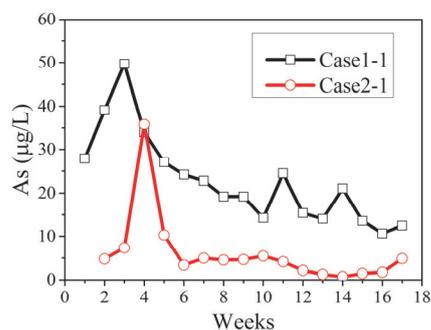


Fig. 3 Total As concentration vs. time (50 mL/week)

Figure 4 shows total As concentration of effluent from the columns in Cases 1-2, 2-2, and 3 at an irrigation rate of 200 mL/week. Total As concentration in Case 2-2 was generally less than that

in Case 1-2 and the environmental standard of As in Japan. The highest total As concentration in Case 2-2 was 17 μg/L at the 4<sup>th</sup> week whereas that in Case 1-2 was 30 μg/L at the 1<sup>st</sup> week. In particular, total As concentration in Case 3 remained almost constant around 2 μg/L and the highest As concentration was decreased to 3 μg/L.

From these results, the river sediment reveals a significant performance of As adsorption. In addition, the covering-soil layer influenced reducing As leaching.

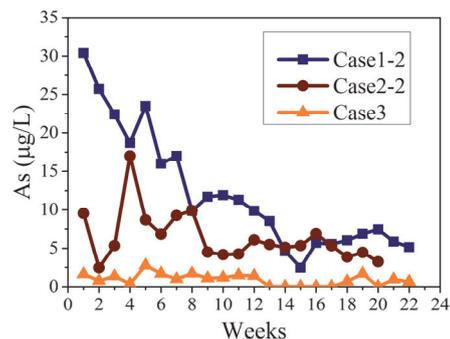


Fig. 4 Total As concentration vs. time (200 mL/week)

## 4. Discussion

To evaluate the effects of adsorption and covering-soil layers on As release, the amount of As released from columns was calculated by the following equation.

$$\text{As leaching amount} = \sum C_i V_i$$

where,  $C$  is As concentration (μg/L),  $V$  is the volume of leachate (L), and  $i$  is the number of effluent collected.

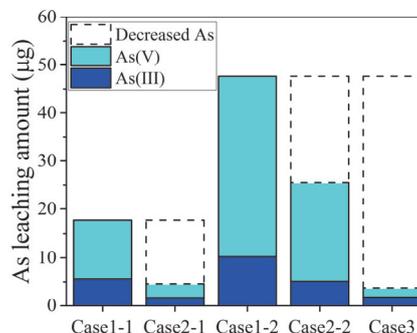


Fig. 5 The amount of As released by considering chemical species

Figure 5 shows the amount of total As released from columns by considering chemical species. The amount of total As released in Cases 2-1 and 2-2 decreased by 74% and 54%, compared with those in Cases 1-1 and 1-2, respectively. The amount of As released in Case 3 decreased by 90% compared with that in Case 1-2. In addition, not only As(V) but also As(III) was adsorbed by the river sediment although the major chemical species of As was As(V) in any case. Furthermore, the leaching of both As(V) and As(III) from the rock layer was reduced by being covered with the river sediment. Therefore, both adsorption and covering-soil layers have significant effects on reducing As leaching.

Figure 6 shows the relationship between As and  $\text{SO}_4^{2-}$  in Cases 1-1 and 1-2. A positive correlation between As and  $\text{SO}_4^{2-}$  was observed. Trace pyrite was also observed as shown in Fig. 2. These indicate that As leaching results from oxidation of pyrite containing As. The data in Cases 2-1 and 2-2 are also plotted in Fig. 6. Only an adsorption layer is not effective in reducing nonreactive  $\text{SO}_4^{2-}$  concentration because the concentration range in  $\text{SO}_4^{2-}$  were almost the same between Cases 1-1 and 2-1, and between Cases 1-2 and 2-2.

By considering the above results, adsorption layer retains As leached from the crushed rock. Moreover, both adsorption and covering-soil layers may reduce oxygen concentration in the rock layer, leading to reducing the rate of oxidation and the leaching concentration of As.

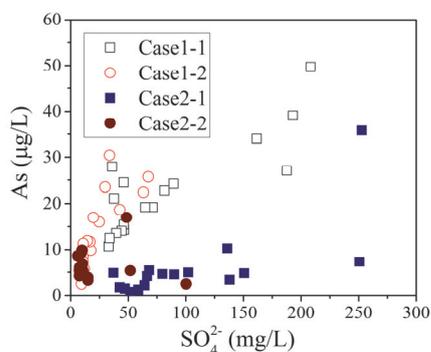


Fig. 6 Total As concentration vs.  $\text{SO}_4^{2-}$  concentration in effluent

The pH values of effluent from the columns in Cases 1-1 and 1-2 were alkaline ranging from 7.7 to 9.7 whereas those from the columns in Cases 2-1 and 2-2 were neutral ranging from 6.9 to 8.0. This means that the adsorption layer has an effect of decreasing pH from alkaline to almost neutral.

## 5. Conclusions

The effects of adsorption and covering-soil layers on As leaching were examined. The findings are summarized as follow:

- (1) The bottom adsorption layer adsorbed As leached from the excavated rock, and reduced the As concentration in the effluent from columns.
- (2) Arsenic concentration in effluent from the column with both adsorption and covering-soil layers was dramatically decreased compared with that without a covering-soil layer.
- (3) Arsenic leaching from the excavated rock results from oxidation of pyrite in the rock used.
- (4) Both adsorption and covering-soil layers have an important role in reducing As release.

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