Study on the Effects of Covering and Adsorption Layers on Immobilizing Arsenic from Hydrothermally Altered Rock

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Introduction

Hydrothermally altered rocks are frequently encountered when tunnels are constructed in Hokkaido, Japan. High concentrations of hazardous elements, such as arsenic (As), are often released from these rocks into the surrounding environments. A massive amount of hydrothermally altered rocks is expected to be produced from the ongoing tunnel construction projects. Improper disposal of these excavated rocks will present a problem, which poses a potential environmental hazard, particularly to soil and groundwater. At present, the excavated rocks are regularly disposed to specially designed landfills to minimize the contact of the rocks with surrounding environments (Katsumi et al. 2001). These methods of disposing, however, are economically infeasible. Thus, factors controlling the mobility of As from hydrothermally altered rocks are needed to be investigated to develop a sustainable technique for disposing of these waste rocks. Recently, several studies have investigated the mechanisms of As migration from hydrothermally altered rocks by using laboratory column experiments. This study aims to expand those previous results by focusing on two concerns: (1) developing a method to demonstrate the effects of water content and oxygen (O_2) concentration in relation to adding covering and adsorption layers on As leaching by introducing water content and oxygen concentration sensors into columns, and (2) modeling of As migration to provide insights into the transport phenomena of As through an unsaturated adsorption layer by using Hydrus-1D.

Effects of Additional Layer(s) on Mobility of Arsenic from Hydrothermally Altered Rock in Laboratory Column Experiments

The mobility of As from hydrothermally altered rocks is generally governed by precipitation, dissolution, adsorption, and desorption reactions, which are highly pH- and redox-dependent (Appelo and Postma 2005; Foster et al. 1998; Savage et al. 2000; Tabelin and Igarashi 2009). Several studies have reported the parameter controlling the mobility of As from hydrothermally altered rocks by using column experiments to mimic the actual disposal. However, the relationship between the conditions of the columns, such as O_2 concentration and water content, and As leaching was not well described by those experimental setups. These two parameters may act as the fundamental key components of As release (Tabelin and Igarashi 2009; Tabelin et al. 201a). Therefore, a more in-depth understanding of the mechanisms is still needed since it can be applied to the development of countermeasures that can be used to minimize the mobility of As from hazardous waste rocks. Herein, we have developed a method to demonstrate the effects of water content and O_2 concentration in relation to adding covering and adsorption layers on As leaching by introducing water content and O_2 concentration sensors into columns. By using the laboratory columns, O_2 concentration and water content were continuously monitored while simulated rain was irrigated. This will allow a better understanding of As migration mechanisms from the rocks together with the development of disposal techniques for hazardous waste rocks.

Materials and Methods

The rock sample used in this study was collected from an interim storage site of a tunnel construction in Nakakoshi, Hokkaido, Japan. The additional layer(s), including river sediment and volcanic ash, were taken from a river located near the waste rock storage site and Otaru town in Hokkaido, respectively. In preparation, the solid samples were air-dried under ambient conditions, crushed, sieved with a 2-mm aperture screen, and completely mixed. Finally, the samples were kept in air-tight containers prior to the use.

The laboratory column setup and dimensions of them are illustrated in Fig. 1. Four cases of column experiments were built and placed under ambient conditions to mimic the actual disposal environment. Three sensors were installed inside each column. Two of them were responsible for measuring volumetric water content (Θ) (WD-3, ARP Corporation, Japan), and the other sensor was used for detecting O_2 concentration (MIJ-03, Environmental Measurement Japan Corporation, Japan). The O_2 concentration sensor was placed between the two water content sensors, which were located at a depth of 5 and 15 cm from the top of the crushed rock layer. Every week, 200 mL of distilled water, equivalent to the average rainfall in Hokkaido, was poured at once to the rain fall simulator at the top of each column, and it gravitationally infiltrated to the packed layer, representing a heavy rainfall (Ministry of Land Infrastructure Transport and Tourism Japan 2010). This irrigation corresponds to the worst case scenario in terms of As leaching (Tabelin et al. 2012). Effluents were collected at the bottom of each column once a week before the next irrigation. Once obtained the effluents, pH, ORP, and EC of the liquid sample were immediately measured, then filtered using 0.45-μm Millex® filters, and stored in an air-tight polypropylene bottle prior to chemical analysis using ICP-AES (ICPE-9000, Shimadzu Corporation, Japan) and cation and anion chromatographs (ICS-1000, Dionex Corporation, USA).
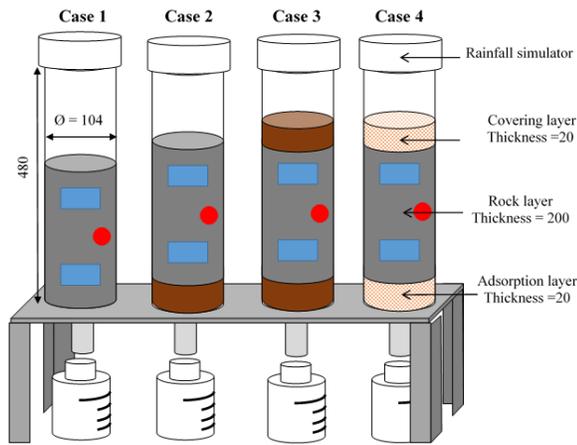
Figure 1 Schematic of the columns; (●) Oxygen concentration sensor, (■) Water content sensor, (■) volcanic ash, and (▨) river sediment (All units are in mm.)

Results and Discussion

Effects of additional layer(s) on water content and oxygen concentration

Figures 2a–d show the change in volumetric water content in cases 1 to 4. During the first few weeks, after irrigation in all cases, the water content rapidly increased, and then remained at higher content, demonstrating the accumulation of water inside the columns. The water content at a deeper rock layer in case 1 was slightly decreased after each irrigation for the first few weeks whereas the water content in the other cases became almost constant regardless of the irrigation. This is probably due to the water retention characteristics of additional layer(s) in cases 2 to 4; covering and adsorption layers can help to prevent rapid evaporation and percolation of water from the rock layer, respectively. In all columns, as time elapsed, the shallower water content fluctuated in accordance with weekly irrigation while almost constant water content was observed in the deeper layer. These results indicate that the water content in the upper rock layer was unsaturated whereas the water content in the lower layer was almost saturated. The degree of fluctuation of the shallower water content in case 3 was less drastic than those in cases of 1, 2, and 4, indicating either the lower porosity distribution around the sensor or the higher saturation state at the shallower layer. The nearly saturated zone in the rock layer was expected to be more in cases 2, 3, and 4 than case 1 due to the presence of the adsorption layer in those cases. Moreover, in case 2, a flat peak of the signal from the shallower sensor was observed from week 9, indicating larger development of the zone with almost saturated water content, caused by development of clogging water pathways in the column.

Figure 3 shows the change in O_2 concentration in cases 1 to 4. The O_2 sensors used in this experiment can detect O_2 concentration in both gaseous and aqueous phases. Initial O_2 concentration was approximately 21% in all the cases, which is equivalent to the average ambient concentration of O_2. Except for case 1, the amount of O_2 gradually decreased before the first collection (week 3 for case 1 and week 4 for

the other cases). After the water content at the deeper rock layer approached saturation, O_2 concentration dramatically decreased and reached almost zero at week 6 in cases 2 and 3, and at week 10 in case 4. On the other hand, in case 1, O_2 concentration gradually decreased until week 10 before exponentially decreasing and reaching almost zero at week 15. These results clearly indicate a negative correlation between O_2 concentration and volumetric water content, meaning that the faster the accumulation of water, the faster the reduction of O_2 concentration. A delay in the reduction among them was observed, which is possibly due to the effects of the adsorption and covering layers. It was only the rock layer in case 1 (without covering and adsorption layers) that led to the slowest accumulation of water among all the cases. This resulted in the slowest reduction of O_2. Moreover, the O_2 concentration was affected not only by water replacement but also by the oxidation of sulfide minerals in the rock. This observation was supported by the slight reduction of O_2 concentration at the position where water content was already stable.
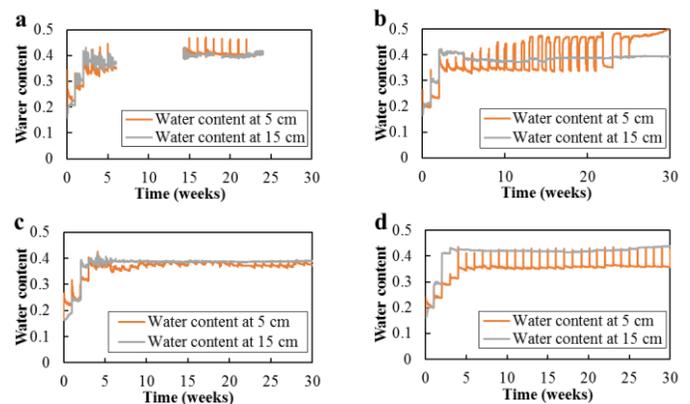

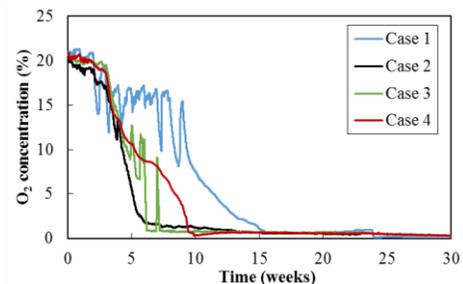Figure 2 Changes in water content; (a) Case 1, (b) Case 2, (c) Case 3, and (d) Case 4

Figure 3 Changes of oxygen concentration

Effects of additional layer(s) on Arsenic Release

Figure 4 shows the change of As concentration in the effluent in cases 1 to 4. The As concentration in case 1 was the highest among all the cases and fluctuated between 19 and 38 μg/L throughout the experiment. On the other hand, the leaching concentration of As in case 4 was higher than 10 μg/L during the first 17 weeks before a sudden decrease in week 19 to below 5 μg/L while, in cases of 2 and 3, it was below the drinking water guideline (10 μg/L) except for the leaching of the second effluent in case 2 (WHO 2011). As mentioned earlier, the presence of additional layer(s) resulted

in faster and larger development of the nearly saturated zone in the rock layer. This played an important role in reducing the mobilization of As because of the following mechanisms: first, when the water was accumulated within the rock layer, it led to a slower diffusion rate of O_2 into the rock layer, and second, the lower O_2 concentration decreased oxidation of sulfide minerals, especially pyrite, which resulted in less As released from the rock. Although the adsorption materials had a negative surface charge, these materials also contributed to the reduction of As levels because they contained substantial amounts of aluminum (Al) and iron (Fe) oxides and their own buffering capacity to lower the pH, resulting in increasing As adsorption by the development of a positive surface charge on the adsorbent. The role of the covering layer is generally to limit the intrusion of water and O_2 from the surroundings into the rock. However, it could not be clearly determined since the effects of water runoff were restricted by using one-dimensional column experiments. Moreover, the movement of water in the rock layer may also be a potential factor affecting the migration of As. In cases 2 and 3, the longer water retention time in the rock layer caused by lower hydraulic conductivity of the adsorption layer may lead to more precipitation of Fe oxy-hydroxide/oxide. Longer water residence time allows more time for water to dissolve Fe from the dissolvable phase (e.g., $Fe_2(SO_4)_3$) and precipitate as Fe oxy-hydroxide/oxide, producing H^+ as a by-product. This might be the result of a very low amount of As leaching in cases 2 and 3 due to the following reasons: the first is that these precipitates have high adsorption affinities toward As (Safiullah et al. 2004; Tabelin et al. 2012), the second is that As can also be co-precipitated with Fe oxy-hydroxide/oxide (Klerk et al. 2012; Ruiping et al. 2007).
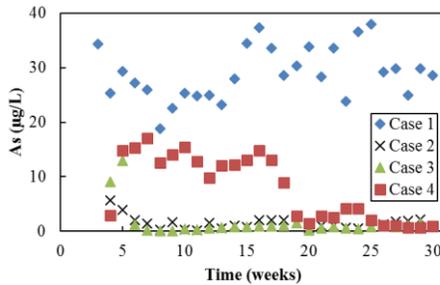

Figure 4 Changes in As concentration with time

Evaluation of Water Movement in a Multilayer Soil Profile Using Hydrus-1D

In searching for alternative materials that are cheap, easy to find in nature, and have the ability to adsorb As leached from the altered rocks for developing a sustainable disposal technique, a variety of analytical and numerical models have been introduced to evaluate the performance in both saturated and unsaturated conditions (Tabelin et al. 2014; Roy et al. 2014; Kofa et al. 2015; Dale et al. 2016). However, the study on the numerical model of As leaching and transport through the unsaturated porous media is still lacking. The water movement is an important factor influencing solute transport. Unlike the flow of water in saturated media, water movement in unsaturated media is much more complicated, which leads to the use of more complex water flow equation in

modeling. This, however, allows us to obtain more accurate prediction. Therefore, before simulating the solute migration, this chapter aims to evaluate the applicability in term of water movement of Hydrus-1D, a software package, in simulating the solute migration from column experiments. The model accuracy was assessed by comparing the observed data with predicted results.

Materials and Methods

Column with additional layers of river sediment in the previous part was selected as a representative since it showed the most complicated As leaching behavior among all cases (Fig. 4).

Hydrus-1D was used to evaluate the transport phenomena of water through the multilayer soil column for a period of 30 weeks. In this study, one-dimensional model could be suitable to describe the flow of water since it was subjected to the transport in column (Simunek et al. 2009).

The movement of water was modeled based on one-dimensional Richard equation as illustrated in Equation (1).

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial h}{\partial z} + 1\right)\right] \tag{1}$$

Where θ is the volumetric water content (cm^3/cm^3), t is time (h), z is the vertical axis (cm), h is the matric head (cm), and $K(\theta)$ is the unsaturated hydraulic conductivity (cm/h). In this simulation, $K(\theta)$ was determined by using the van-Genuchten relationship as shown below:

$$K(\theta) = K_s S_e^{\ l}\left[1 - \left(1 - S_e^{\frac{1}{m}}\right)^m\right]^2 \tag{2}$$

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} \tag{3}$$

$$m = 1 - \frac{1}{n}, n > 1 \tag{4}$$

where the effective saturation (S_e) can be determined by:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{5}$$

and θ_s is the saturated water content (cm^3/cm^3), θ_r is the residual water content (cm^3/cm^3), K_s is the saturated hydraulic conductivity (cm/h), and α, n, and m are fitted parameters determining the shape of the soil water retention curve. The combination of Equations (1) through (5) describes the one-dimensional water movement in both vadose and saturated zones.

The initial condition was used as a fixed water content, measured by the water content sensors. According to the experimental setup, the irrigated water was forced to flow vertically in one-dimension, surface water runoff was negligible, and a flow system existed as a free-outflow boundary. Thus, the upper boundary condition was selected

as the atmospheric boundary with a hypothetical surface layer thicker than the amount of irrigation (>2.4 cm) to represent zero surface water runoff. The lower boundary condition was selected as a seepage face with a specific head. The matric potential was varied to calibrate the model.

Results and Discussion

Water movement was simulated to fit the observed results as illustrated in Fig 5. Hydrus-1D could not simulate the water movement at the beginning of the experiment where the water content was not in the domain of the van-Genuchten equation ($\Theta_r = 0.27$ and $\Theta_s = 0.44$). However, this did not have a significant effect on the modeling of the solute transport since there was no effluent leaching out from the column during this period. In this experiment, water was first irrigated to air-dried samples and thus it was just filled the pores from the air-dried to field capacity (Θ_r) conditions before it started to move gravitationally out of the column (SSSA 1997). Most of the observed values matched well with the simulated results from the point where the water content was within the range of Θ_r and Θ_s. The higher observed data from the lower sensor during the first few weeks probably occurred due to an effect of the unequal hydraulic conductivity of the rock and river sediment. This caused the water to continue accumulating in the rock layer to some extent before flowing down to the layer of river sediment. The inaccurate prediction at the end of the simulation may occurr due to the development of clogging water pathways at the layer below the lower sensor. Although some differences occurred at the beginning and the end of the simulation, Hydrus-1D could predict the transient water movement with high accuracy most of the time. This suggests the capability of Hydrus-1D in simulating the reactive solute transport with accurate transient water movement.
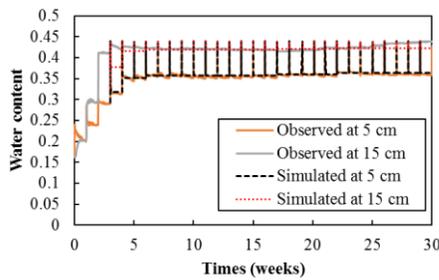

Figure 5 Simulation of water movement using Hydrus-1D

Modeling and Evaluating the Performance of River Sediment on Immobilizing Arsenic from Hydrothermally Altered Rock in Laboratory Column Experiments with Hydrus-1D

The discussion on the capability of Hydrus-1D in modelling of the water movement in the column with a multilayer soil profile was done in the previous part. After approving the capability of Hydrus-1D, performance of the unsaturated river sediment on immobilizing As from hydrothermally altered rock is evaluated. In order to achieve this, Hydrus-1D was used to simulate the solute transport through the unsaturated adsorbent in case 4 with the input of

water movement from the previous part. The characteristics of As migration through the unsaturated adsorbent was assessed based on experimental and simulation results. This study would help in the development of a sustainable way of disposing the hazardous waste rocks.

Materials and Methods

After 30 weeks of experimentation, all columns were disassembled. The rock layer was divided into 4 equal portions (5 cm thick) while both covering and adsorption layers were sectioned in half (1 cm thick). Then, the sectioned samples were air dried under ambient conditions and separately kept in air-tight containers prior to the leaching experiments. The leaching experiments were conducted by mixing 3 g of the solid sample with 100 ml of 1 M hydrochloric acid (HCl) at 200 rpm for 2 hours. The suspensions were then filtered using 0.45 µm Millex®filters (Merck Millipore, USA). Finally, all filtrates were stored at 6ºC prior to chemical analysis using ICP-AES (ICPE-9000, Shimadzu Corporation, Japan).

The As transport through the unsaturated adsorption layer (river sediment) was simulated using the one-dimensional advection-dispersion with retardation and first-order decay equation.

$$\frac{\partial \theta R c}{\partial t} = \frac{\partial}{\partial z}\left[\theta D^w \frac{\partial c}{\partial z}\right] - \frac{\partial q c}{\partial z} + Fc \qquad (6)$$

The retardation factor (R) is defined by;

$$R = 1 + \frac{\rho K_d}{\theta} \qquad (7)$$

where ρ is the bulk density (g/cm³), K_d is the distribution coefficient (linear adsorption isotherm coefficient), C is the solute concentration (mmol/cm³), D^w is the solute dispersion coefficient for the liquid phase (cm²/h), q is the Darcian fluid flux density (cm/h), and F is the first-order decay term (1/h).

The solute transport was simulated with an initial As concentration of zero in the adsorption layer (fresh adsorbent). The upper boundary condition was set for a concentration flux where the concentration of As can be specified. On the other hand, zero concentration gradient (no change in concentration) was chosen as the lower boundary condition since there was no generation or leaked of As along the way from the adsorption layer to the container. The model calibration of the solute transport was done by adjusting two parameters including distribution coefficient (K_d) and first-order decay constant (F). The irrigation and input concentration of As were considered based on the results from the previous part and the average As leaching concentration from case 1 (30 µg/L), respectively.

Results and Discussion

The leaching experiments of the post experimental soil samples were performed to investigate whether or not the precipitation of Fe oxy-hydroxide/oxide was formed and

retained inside the column. The leaching concentrations Fe with depth in cases 1 and 4 are shown in Figs. 6a and b, respectively. The concentrations of Fe leached from the rock were almost identical in all depths and in both columns, demonstrating no precipitation of Fe compounds in the rock layer. Meanwhile, the concentration of Fe in the leachates from the adsorption layer was significantly higher than those from the covering layer. These results confirm the precipitation of Fe oxy-hydroxide/oxide in the river sediment. Consequently, As can be immobilized by co-precipitation with and/or adsorption onto this newly precipitated Fe compounds (Klerk et al. 2012).
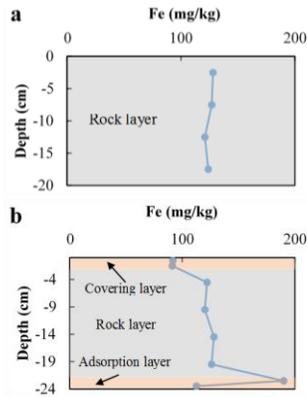

Figure 6 Changes in leaching concentration of Fe with depth: (a) case 1 and (b) case 4

Hydrus-1D was used to simulate the reactive transport of As through the adsorption layer. The simulation was done by using the advection-dispersion with retardation and first-order decay equation (Equation (6)) with an assumption of an equilibrium solute transport model. The equilibrium assumption for the solute transport was made due to the fact that As concentrations in the effluents collected at four different times during the week were almost identical. In other words, the flow was slow enough for the adsorption to reach equilibrium.

Figure 7 shows comparison between simulated results of As migration and observed ones. The leaching behavior of As was divided into 3 periods. First, when the level of As rapidly increased during the first few weeks and then fluctuated slightly with the As concentration higher than drinking water standard (10 µg/L) (WHO 2011) prior to week 17 in the second period. In the last period, a sudden decrease of As level occurred and it remained below 5 µg/L. The modeling was done varying two solute transport parameters, K_d and F. The values of the fitted parameters at different periods are listed in Table 1. First, F was given as a constant equal to 0.01 1/h to adjust the plateau level (at approximately 15µg/L). The K_d was then varied to fit the breakthrough characteristic of As. The value of F remained at 0.01 1/h until week 17 before increasing to 0.06 1/h in which it brought the As concentration down and maintained the leaching concentration at around 3 µg/L from weeks 19 until the end of the simulation.

The simulated results reveal that the mobility of As at the beginning was mainly controlled by K_d. Thus, the major

mechanism retarding the mobility of As in this period was expected to be a reversible adsorption onto the river sediment. After that, the first-order decay constant played a role in maintaining the leaching concentration of approximately 15 µg/L prior to week 17. This likely represents the depletion of As from such phenomena as faster reduction and slower diffusion of O_2 into the rock layer and co-precipitation and adsorption onto newly precipitated Fe oxy-hydroxide/oxide. As time elapsed, the first order decay contributed more significant effect on As releasing behavior. This illustrates further depletion of As likely due to the significantly lower generation by oxidation of sulfide mineral in the rock layer. During this period, the major mechanism of As generation shifted from dissolution to oxidation. This can be explained using the leaching behavior of sulfate (SO_4^{2-}), one of the major coexisting ions (Fig. 8). The SO_4^{2-} concentration in case 4 exponentially decreased and then stayed stable at low concentration afterwards. The rapid decrease of SO_4^{2-} concentration indicates the release of As from both soluble and oxidizable phases. However, the release of As from the soluble phase decreased with time, suggested by the reduction of a flushing-out trend. Therefore, the combination of the allocation of the As generation mechanism and very low O_2 concentration in the rock layer led to a significant reduction of As generation in the last period. In addition, as time elapsed, Fe oxy-hydroxide/oxide continued to precipitate onto the surface of the river sediment, resulting in a higher surface area of the newly precipitated adsorbent over time. Consequently, a higher chance of As being adsorbed onto these newly precipitated materials can be expected.

Table 1 Fitted parameters

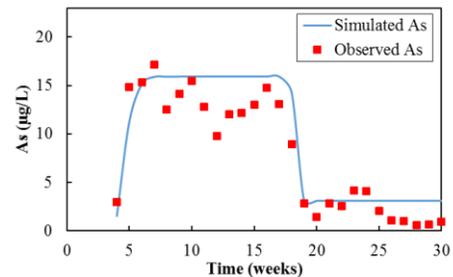| Period	K_d (ml/g)	F (1/h)
1st	10	0.01
2nd	10	0.01
3rd	10	0.06

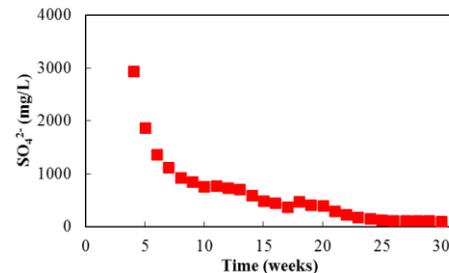Figure 7 Simulation of As breakthrough in case 4 using Hydrus-1D

Figure 8 Leaching behavior of SO_4^{2-} in case 4

Conclusion

This dissertation was conducted with the main objective of evaluating the effects of additional layer(s) on immobilizing As from hydrothermally altered rock. Several laboratory experiments and computer simulations were performed in order to achieve this goal.

Four cases of laboratory column experiment were carried out. Oxygen and water content sensors were installed into the rock layer of every column at the same position. Negative correlation between O_2 concentration and volumetric water content was clearly observed due to the replacement of air by water. Additional layer(s) led to faster and larger development of the zone with higher water content. The development of this zone resulted in the reduction of oxidation of As-bearing minerals due to slower diffusion of air into pore water. The adsorption layer located underneath the rock layer also contributed to the retarding of As since it contained considerable amounts of Fe and Al oxide. Moreover, a lower water flow rate caused by the use of low hydraulic conductivity covering and adsorption layers may lead to higher precipitation of Fe oxy-hydroxide/oxide in the adsorption layer. This precipitate was reported by many studies to have abilities to co-precipitate as well as adsorb As. As a result, the columns with additional layer(s) had a significant effect on lowering the migration of As from the rock layer.

Hydrus-1D was used to investigate the water movement and reactive transport of As through an unsaturated adsorption layer (river sediment). It was successfully proved that Hydrus-1D had ability to simulate the reactive transport of As with high level of accuracy in term of transient water movement. Then the breakthrough curve of As was fitted by adjusting two solute transport parameters of K_d and F. Based on the analysis of experimental and simulation data, the leaching behavior of As through the river sediment was divided into 3 periods. From weeks 1-5, the As was potentially retarded by the adsorption onto minerals initially contained in the river sediment. The second period, weeks 5-17, the reduction of oxidation of As bearing-minerals, irreversible adsorption, and the adsorption onto newly precipitated Fe oxy-hydroxide/oxide played a major role affecting the mobility of As. In the last period, the major mechanism of As generation shifted to the oxidization of As-bearing minerals. Consequently, the generation of As significantly decreased since the O_2 concentration in the rock layer was low. Additionally, the surface area of the newly precipitated Fe oxy-hydroxide/oxide increased over time, resulting in more chance of As to be retarded by these potential adsorbents. In conclusion, significant amounts of As were reduced by the use of river sediment.

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