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## Leaching of arsenic from hydrothermally altered rock in laboratory saturated-column experiments

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### Abstract

This study describes the leaching of arsenic (As) from hydrothermally altered rock under saturated-column conditions. The altered rock sample used is predominantly composed of silicate minerals (*i.e.*, quartz and plagioclase), with chlorite and calcite as minor minerals, and pyrite in trace amounts. It contains 23.6 mg/kg of As, which is about twice as high as the average As content of sedimentary rocks. The pH of all effluents were alkaline ranging from 7.8 to 10 while the measured Eh values ranged from +250 – +400 mV indicating oxic conditions throughout the duration of the experiment. The leaching curve of As under saturated-flow conditions featured a prominent concentration peak of 134 µg/L around day 0.65. After reaching this peak, the concentration decreased with time and stabilized in the range of 17 – 25 µg/L after ca. day 10. In contrast, the leaching curves of more conservative ions like Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> resembled distinct flushing-out trends. These results indicate that the leaching behavior of As under saturated-column conditions is non-conservative, and the altered rock is capable of releasing significant amounts of As for a long period.

Keywords: Hydrothermal alteration, Arsenic, Column experiments

### 1. INTRODUCTION

A large number of hot springs or “onsen” is found throughout Japan, a consequence of many active volcanoes distributed all over the country. However, the active volcanic strata beneath the country also caused large quantities of rocks to undergo hydrothermal alteration. Hydrothermally altered rocks are formed when the hot and often mineralized hydrothermal fluid/solution, which comes directly from magmatic intrusions or is formed because of the superheating of ground/sea water after getting in contact with underground heat sources, interacts with the surrounding rocks through fractures and fissures. Because hydrothermal fluids/solutions are generally very corrosive, portions of the host rock located near the center of the alteration are dissolved and new minerals are formed in its place (Pirajno 2009). In addition, transformation of the host rock could extend several meters from the center of alteration (Tabelin *et al.* 2012a). Ore deposits containing valuable metallic elements (*e.g.*, Au, Ag and Cu) are formed via this process in certain exceptional cases when the hydrothermal fluid is highly mineralized. In most cases, however, the hydrothermal fluids interacting with the host rock are less mineralized, which causes little enrichment of valuable metallic minerals but substantial changes in the chemical and mineralogical properties of the surrounding rock. On an environmental and health

perspective, the most important change that occur in the host rock during hydrothermal alteration is its enrichment with As and other hazardous elements like heavy metals. Most of this enrichment occurs within precipitated pyrite grains and not with the aluminate-silicate matrix of the rock (Tabelin *et al.* 2012a). Precipitated pyrite grains during hydrothermal alteration could contain as much as 1.7 wt.% (10,700 mg/kg) As and 0.26 wt.% (2,600 mg/kg) Pb (Tabelin *et al.* 2012a). Therefore, hydrothermally altered rocks are potential sources of As contamination and should be disposed of properly.

Hydrothermally altered rocks have been extensively studied especially with regards to the formation and characterization of ore forming minerals (Aiuppa *et al.* 2006; Allen and Hahn 1994; Halbach *et al.* 1993; Horton *et al.* 2001; Huston *et al.* 1995; Ostwald and England 1977) as well as the evolution of toxic elements including As and heavy metals from mine pit lakes (Davis and Ashenberg 1989; Davis *et al.* 2006; Eary 1998; Levy *et al.* 1997; Savage *et al.* 2009; Tempel *et al.* 2000). However, very few researches have been conducted regarding the mobilization of As and other hazardous elements from altered rocks excavated during tunnel construction. We have published works highlighting the importance of pH, redox potential (Eh) and atmospheric O<sub>2</sub> and CO<sub>2</sub> on the leaching of As and Pb from these altered rocks (Igarashi *et al.* 2008; Tabelin and Igarashi 2009;

Tabelin *et al.* 2010; Tabelin *et al.* 2012a, 2012b, 2012c, 2012d). In addition, the leaching of As changes with time and is highly dependent on the mineral composition of the altered rock. For example, As is easily leached out from altered rocks with high contents of pyrite and low buffering capacity because of the strongly acidic pH of the leachate (Tabelin *et al.* 2012d; Tatsuha *et al.* 2012). However, altered rocks with low pyrite content and high buffering capacity (*i.e.*, high content of carbonate minerals like calcite) have leaching curves strongly influenced by adsorption and precipitation reactions (Tabelin *et al.* 2012b, 2012c, 2012d). Although we found that water infiltration is important in the migration of As through the rock because of its strong influence on the leachate pH and the extent of Fe-oxyhydroxides precipitation under unsaturated-saturated conditions (Tabelin *et al.* 2012b, 2012c), the leaching of As and the effects of pH, Eh and coexisting ions under saturated-flow conditions are still unclear. Therefore, this study evaluated the leaching behavior of As and the evolution of pH, Eh and coexisting ions under saturated-column conditions. In addition, characteristics of the water flow and their influence on the leaching of As and coexisting ions were evaluated. Finally, the authors investigated the effects of coexisting ions like  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and Fe on the migration of As under saturated-column conditions.

## 2. MATERIALS AND METHODS

### 2.1 Hydrothermally altered rock

The rock sample used in this study was excavated from a tunnel project for the national highway connecting the cities of Asahikawa and Monbetsu. This tunnel was constructed in the Nakakoshi area of Kamikawa Province, Hokkaido, Japan. Hydrothermally altered rock was excavated in the first 175 m of the tunnel. The alteration was accompanied by a mineralized zone with a maximum width of 2.5 m, composed of quartz-pyrite veins and veinlets, and a strongly altered andesite dike with a width of 4 m (Tabelin *et al.* 2012b). The hydrothermal alteration in this area is characterized by silicification, pyritization and argillic alteration of kaolinite resulting in high As abundance of the rock (up to 513 mg/kg) (Tabelin *et al.* 2012b). The excavated rocks from the tunnel project were stored in interim disposal sites prior to their final disposal. Sampling was done at random points around this interim storage area using hand shovels. The rock sample was brought back to the laboratory, air dried, crushed using a jaw crusher and sieved through a 2 mm aperture screen. The <2 mm fraction was collected, mixed thoroughly and stored in airtight containers to minimize its exposure to moisture. The altered rock sample is composed predominantly of quartz and plagioclase, with calcite as a minor mineral

constituent and pyrite in trace amounts. The bulk As content of the rock is 23.6 mg/kg, with low sulfur content of 0.20 wt.% (Tabelin *et al.* 2012b). Based on the results of sequential extraction, majority of As in this rock is found together with sulfides at 55.2% of the total As content of the rock (Tabelin *et al.* 2012b). Substantial amounts were also measured in association with the exchangeable phases (17.9%), carbonates (2.3%) and reducible fraction (*i.e.*, Fe-Mn oxides) (2.4%). The remainder (22.2 % of the total As) is found in the residual phase, which is considered immobile under normal geochemical conditions. The <2 mm fraction used during the column experiment is classified as clayey sand, a mixture of 70.4% sand, 22.3% silt and 7.3% clay (Tabelin *et al.* 2012b). The specific gravity and water content of the rock sample are 2.731 and 0.5 wt.%, respectively (Tabelin *et al.* 2012c).

### 2.2 Column experiments

The column apparatus used in this study is made of glass that has a length of 30 cm and an inner diameter of 2.54 cm. The thickness of the column rock bed was 20 cm with a bulk density of 1.62 g/cm<sup>3</sup>. Baffles were placed on both ends of the rock bed to minimize the formation of dead zones and flow variations around the ends of the column. These baffles were 5 cm thick and composed of spherical glass beads ca. 2 mm in diameter. The rock bed and baffles were separated by glass filters with a thickness of ca. 1 mm. Deionized water (18Ω·cm) taken from a Milli-Q® Integral Water Purification System (Merck Millipore, USA) was introduced underneath the column and forced to flow upwards using a peristaltic pump (Eyela cassette tube pump SMP-21, Tokyo Rikakikai Co., Ltd., Japan) at an average flow rate of 0.22 cm<sup>3</sup>/min. Effluent samples were collected at 240 min-intervals using an automated fraction collector (Eyela fraction collector DC-1200, Tokyo Rikakikai Co., Ltd., Japan). The weight of each effluent sample was measured followed by the determination of its pH, Eh and electrical conductivity (EC). After these measurements, the effluents were filtered through 0.45 μm Millex® sterile membrane filters (Merck Millipore, USA) and stored at 6°C prior to the chemical analyses.

A tracer test using potassium bromide (KBr) solution was conducted after 22 days. The tracer solution was prepared from reagent grade KBr powders (Wako Pure Chemical Industries Ltd., Japan) and Br<sup>-</sup> concentration of the bulk tracer solution was determined prior to the test. For the interpretation of the tracer test results, the pore volume (PV) was calculated from (American Society for Testing Materials, 1989):

$$PV = V - \frac{M}{[(1 + w) * S * D]}$$

where,  $PV$ : pore volume ( $\text{cm}^3$ ),

$V$ : as-packed volume ( $\text{cm}^3$ ),

$M$ : as-packed weight, including moisture (g),

$w$ : moisture content (unit less),

$S$ : specific gravity, and

$D$ : density of water ( $\text{g}/\text{cm}^3$ )

Transport parameters were estimated from the tracer test results using the one-dimensional advective-dispersive transport capability of PHREEQC (Parkhurst and Appelo, 1999).

### 2.3 Chemical analyses

Effluent samples with As concentrations greater than  $100 \mu\text{g}/\text{L}$  were measured directly using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE 9000, Shimadzu Corporation, Japan) while those with As concentrations less than  $100 \mu\text{g}/\text{L}$  were first pretreated and then measured using a hydride generator attached to the ICP-AES. For the pretreatment of effluents with low As concentrations, 15 ml of 12 M hydrochloric acid (HCl), 2 ml of 20% potassium iodide (KI) solution, and 1 ml of 10% ascorbic acid solution were added to 30 ml of effluent, diluted with deionized water to 50 ml and mixed thoroughly using a magnetic stirrer. Analyses of pretreated samples were done at least 3 hours after the pretreatment to facilitate the complete reduction of As[V] to As[III]. Important coexisting ions like  $\text{Ca}^{2+}$  and Fe with concentrations greater than  $0.1 \text{ mg}/\text{L}$  were determined using the ICP-AES. For very low concentrations of these coexisting ions ( $< 0.1 \text{ mg}/\text{L}$ ), an ultrasonic aerosol generator attached to the ICP-AES was used. Sulfur in the first 20 effluent samples collected were measured using an anion chromatograph (ICS-1000, Dionex Corporation, USA) and was found predominantly in the form of sulfate ( $\text{SO}_4^{2-}$ ). Thus, for faster and easier determination of  $\text{SO}_4^{2-}$ , the ICP-AES was used later on in the study. Bromide concentrations during the tracer test were also measured using anion chromatography. The standard ICP-AES method (i.e., without attachment) has a margin of error of ca. 2–3% while more sensitive hydride generation and ultrasonic aerosol generator methods have uncertainties of ca. 5%. The detection limits of the standard ICP-AES method for Ca, Fe, S and As are approximately 0.1, 2, 0.02, and  $40 \mu\text{g}/\text{L}$ , respectively. The hydride generation method for As has a detection limit of  $0.1 \mu\text{g}/\text{L}$  while the ultrasonic aerosol generator attachment has a detection limit of  $1 \mu\text{g}/\text{L}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 Evolution of pH, Eh, EC and the concentrations of As, $\text{Ca}^{2+}$ , $\text{SO}_4^{2-}$ and Fe

The changes in the effluent pH and Eh with time are shown in Figure 1. The pH trend in the saturated column resembled a recurring “wave-like” pattern. This pattern is clearly visible at time intervals of 3–6, 7–9, and 10–12 days, which can be described as a sudden decrease in the pH that is immediately followed by a gradual increase. Although the pH curve under saturated conditions appeared erratic, the measured values were always found between pH 7.8 and 10, indicating that the conditions range from circumneutral to alkaline. The Eh values of the effluents have a less erratic pattern compared to the pH (Figure 1). The measured Eh ranged between +250 and +400 mV, which suggests that the saturated rock bed system is under oxidizing conditions.

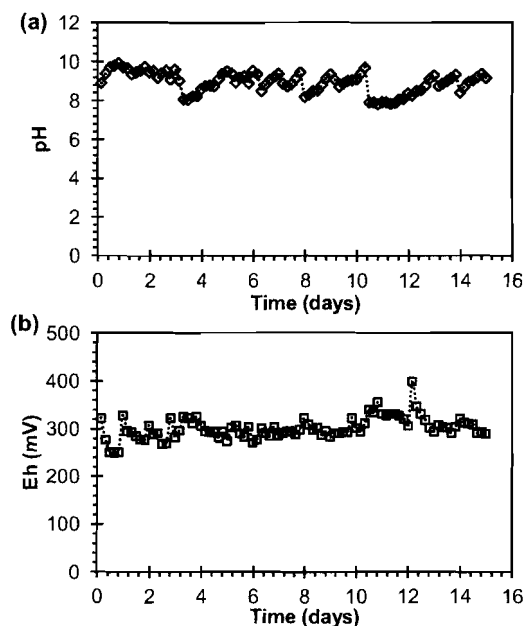


Figure 1. Evolution of pH and Eh under saturated-column conditions; (a) pH change with time, and (b) Eh change with time.

The EC,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  curves are illustrated in Figure 2. The EC value of a liquid sample is a rough indicator of its total amount of dissolved ions, that is, very high EC values indicate relatively high concentrations of cations and anions while very low EC values mean almost pure water. The highest EC value ( $2,840 \mu\text{S}/\text{cm}$ ) was measured in the first effluent sample, which decreased rapidly with time and stabilized in the range of  $38 - 70 \mu\text{S}/\text{cm}$  after ca. 1.6

days. The leaching curves of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  had flushing-out trends similar to that of the EC, that is, the initial concentrations of these ions were very high at the start of the experiment, rapidly decreased and stabilized with time. The concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  at the start of the experiment were relatively high at 95.3 and 630 mg/L, respectively. These values decreased by ca. 20-fold for  $\text{Ca}^{2+}$  and 70-fold for  $\text{SO}_4^{2-}$  in a short span of 1 to 2 days. Little change was observed in the concentrations of these two ions after two days, indicating that apparent equilibrium in terms of the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations was rapidly achieved. In addition, the flushing-out trend of the EC indicates that substantial amounts of soluble phases are found in the altered rock. Furthermore, these soluble phases are most likely mineral phases of Ca and  $\text{SO}_4^{2-}$  like gypsum as suggested by the similar trends in the  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and EC curves.

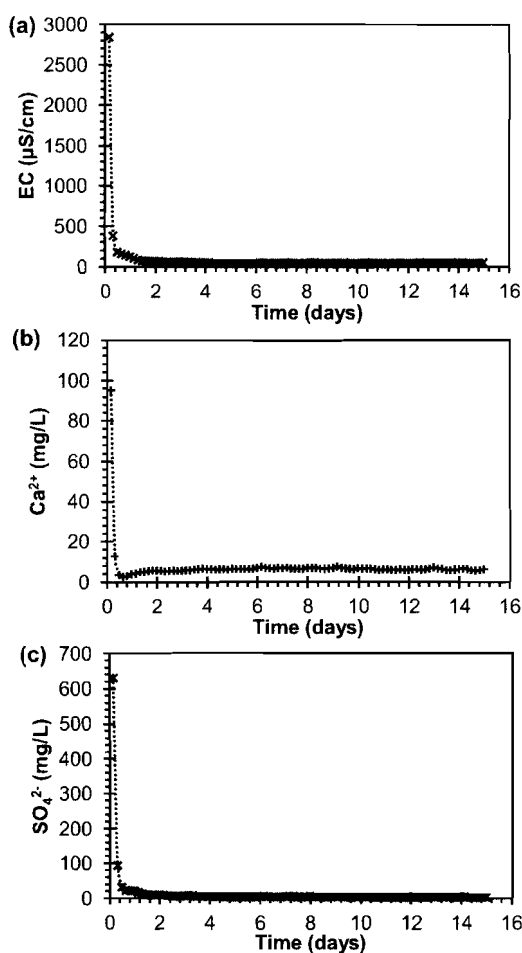


Figure 2. Evolution of EC,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  under saturated-column conditions; (a) EC change with time, (b)  $\text{Ca}^{2+}$  concentration change with time, and (c)  $\text{SO}_4^{2-}$  concentration change with time.

The leaching behavior of As with time under saturated conditions is shown in Figure 3(a). Initially the concentration of As was 32 µg/L, which increased with time until 134 µg/L was reached that corresponded to the maximum leaching concentration during the experiment. After this, the concentration of As decreased gradually reaching apparent equilibrium ca. 9 days after the observed As concentration peak. The concentrations of As in the effluents after apparent equilibrium ranged from 17 to 25 µg/L, which were still higher than the drinking water standard of Japan (10 µg/L). Concentrations of Fe were only measurable in the first 11 effluent samples collected. As illustrated in Figure 3(b), the leaching trend of Fe had a distinct concentration peak during the first two days of the experiment similar to that of As. The Fe concentration peak was observed around day 0.81 amounting to 0.046 mg/L. The appearance of this Fe concentration peak was observed immediately after that of As (Figure 3). From day 2 until the end of the experiment, the leaching concentration of Fe was always less than 0.001 mg/L.

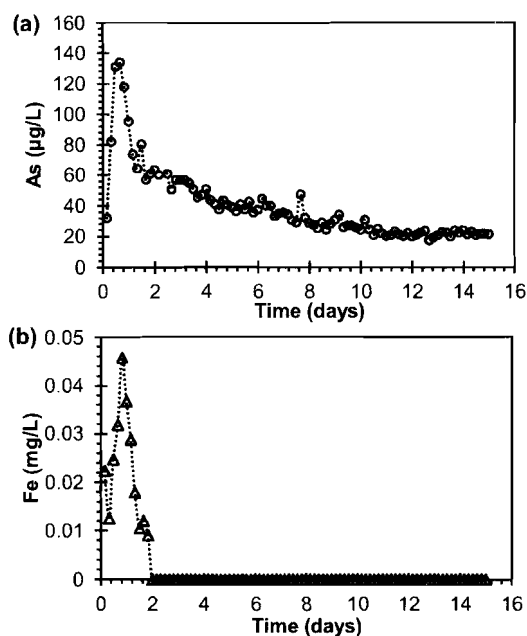


Figure 3. Evolution of As and Fe under saturated-column conditions; (a) As concentration change with time, and (b) Fe concentration change with time.

### 3.2 Tracer test and water flow characteristics

Figure 4 shows the results of the tracer test using  $\text{Br}^-$ . The plots and curves in this figure represent the experimental data and calculated results, respectively. Dispersivity ( $\alpha$ ) of the rock bed was estimated by fitting calculated curves based on the one-dimensional

advection-dispersion equation to the experimental results. The average linear water velocity used in the model was equal to 56.9 cm/h, which was calculated from measured volumetric flow rate. Based on our calculations, the dispersivity of the rock bed with bulk density of 1.62 g/cm<sup>3</sup> and porosity of 40.7% ranged from 1 to 2 cm. This relatively low dispersivity in the column indicates that water flow was not facilitated by preferential flow or “channeling” and the transport of conservative ions like Br<sup>-</sup> could be explained by the simple advection and dispersion.

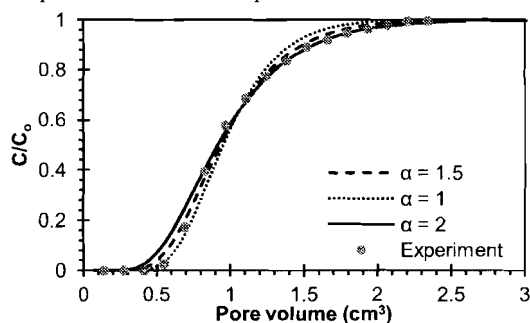


Figure 4. Br<sup>-</sup> concentration change during the tracer test. Plots denote the experimental results while the curves represent calculated values using dispersivities ( $\alpha$ ) of 1, 1.5 and 2 cm.

### 3.3 Effects of pH, Eh and coexisting ions on As leaching under saturated conditions

As illustrated in Figure 3, the leaching of As from the altered rock under saturated-column conditions could be divided into two phases: an early stage characterized by rapid concentration increase and decrease forming a distinct peak and a later stage where the concentration of As gradually decreased and stabilized. This observed As leaching behavior under saturated-column conditions is identical to those reported in our previous papers under unsaturated-saturated column conditions (Tabelin *et al.* 2012b, 2012c). Dramatic changes in the concentrations of Fe, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> were also observed during the first two days of the experiment in conjunction with that of As. To better understand the effects of these parameters on the leaching of As under saturated conditions, statistical analysis was used to compute the correlations of As with each of the parameters. This was done by dividing the results into two groups: first group (early stage) composed of the results during the first two days and second group (later stage) comprised of all the data after day 2. The results of the statistical analysis are shown in Tables 1 and 2 for the early and later stages, respectively. During the first two days of the experiment, As leaching had a strongly positive and statistically significant correlation with pH, indicating that As leaching is enhanced at higher pH under alkaline conditions (Table 1). This could be attributed to enhanced desorption of As as

well as the increased oxidation of pyrite under these conditions (Evangelou, 1995; Tabelin and Igarashi, 2009). In contrast, As and Eh had a moderately negative and statistically significant correlation, which means that the leaching of As tend to increase with decreasing Eh. However, because the Eh values did not change dramatically and were always under oxidizing conditions during the experiment, this correlation could be a consequence of the decrease of Eh with increasing pH. This means that slight changes in the Eh of the system do not dramatically affect the leaching of As. Calcium ions also had a strong effect on the leaching of As based on the results of the statistical analysis. The strongly negative and statistically significant correlation between As and Ca<sup>2+</sup> indicates that higher Ca<sup>2+</sup> concentration minimizes As leaching most probably due to the formation of more positively charged mineral surfaces that enhances As adsorption (Rahnemaie *et al.*, 2006; Stachowicz *et al.*, 2008). For Fe and SO<sub>4</sub><sup>2-</sup>, their correlations with As were statistically insignificant.

Table 1. Correlation of As with pH, Eh, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and Fe during the first 2 days of the experiment

Sample	a	b	R	N	p
As vs pH	7.44	0.057	0.82	12	<0.005
As vs Eh	558	-0.156	0.68	12	<0.025
As vs Ca <sup>2+</sup>	21,028	-1.87	0.80	12	<0.005
As vs SO <sub>4</sub> <sup>2-</sup>	3092	-1.11	0.37	12	NS
As vs Fe	0.002	0.587	0.45	11	NS

$y = ax^b$ . y: As concentration in the leachate, x: pH, Eh, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> or Fe concentration in the leachate, a,b: constants, R: correlation coefficient, N: number of data points, p: statistical significance, and NS: not statistically significant.

In the later stages of the experiment close to apparent equilibrium, the leaching of As was still affected by pH, Eh and coexisting ions but to a much lesser degree. For example, only a moderate positive correlation was found between As concentration and pH. Similarly, the effect of Ca<sup>2+</sup> concentration on As leaching became negligible, which could be attributed to the relatively low and nearly constant Ca<sup>2+</sup> concentration around this period. Surprisingly, SO<sub>4</sub><sup>2-</sup> had a strongly positive and statistically significant correlation with the concentration of As in this period, which is very different from that observed in the first two days of the experiments. Although SO<sub>4</sub><sup>2-</sup> had been reported to slightly enhance As desorption at high concentrations (>250 mg/L) (Jeong *et al.*, 2007; Zeng 2004), this was not the case during the experiment. In the later stages of the experiment, SO<sub>4</sub><sup>2-</sup> concentration ranged from 2 – 9 mg/L that is very low to have significant competitive effects on As adsorption. Thus, the increase in As and SO<sub>4</sub><sup>2-</sup> concentrations during this period were probably the result of enhanced pyrite oxidation due to the pH increase.

Table 2. Correlation of As with pH, Eh, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> after 2 days of the experiment

Sample	a	b	R	N	p
As vs pH	7.37	0.053	0.30	78	<0.01
As vs Eh	410	-0.088	0.45	78	<0.005
As vs Ca <sup>2+</sup>	6.53	-0.006	0.03	78	NS
As vs SO <sub>4</sub> <sup>2-</sup>	0.476	0.664	0.77	78	<0.005

$y = ax^b$ , y: As concentration in the leachate, x: pH, Eh, Ca<sup>2+</sup> or SO<sub>4</sub><sup>2-</sup> concentration in the leachate, a,b: constants, R: correlation coefficient, N: number of data points, p: statistical significance, and NS: not statistically significant.

#### 4. CONCLUSIONS

Hydrothermally altered rock excavated during a road-tunnel construction project contain substantial amounts of As. The leaching behavior of As under saturated-column conditions was evaluated in this study and could be divided into two distinct regions: an early stage and a later stage. The early stage was quite short, characterized by rapid increase and decrease of As concentration, measurable concentrations of Fe and flushing-out trends of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. On the other hand, the leaching of As in the later stage decreased gradually followed by stabilization. Little change was also observed in the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> during this period. Dissolution of the soluble phases present in the altered rock was responsible for the large variations in the leaching behavior of As as well as those of the coexisting ions during the early part of the experiment. After reaching apparent equilibrium, the rock continued to release As, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> due to the continued oxidation of pyrite and dissolution of calcite. In addition, majority of the Fe released as a consequence of pyrite oxidation is also re-precipitated because of alkaline conditions as indicated by the very low Fe concentrations in the effluents at this period. Therefore, a portion of the released As is re-adsorbed onto these Fe-precipitates. However, this process is limited because of the low concentration of these precipitates in the rock and the enhanced desorption of As under alkaline conditions. Because of this, the rock will continue to release As at amounts greater than the drinking water standard of Japan.

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