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Chemical Forms of Arsenic and Selenium Leached from Mudstones

Toshifumi IGARASHI¹, Ryosuke SASAKI², and Carlito B. TABELIN¹

¹ Department of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
² Department of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Abstract

Batch leaching experiments were conducted to elucidate the leaching behaviors and chemical forms of arsenic (As) and selenium (Se) from excavated mudstones. The results showed that As and Se concentrations in the leachate were higher than the environmental standards (10 μg/L), and that the major chemical forms of As and Se were arsenate (As(V)) and selenate (Se(VI)), respectively. Consecutive batch leaching experiments showed that the major chemical form of As was As(V) regardless of the number of extraction whereas that of Se changed from Se(VI) to selenite (Se(IV)) with the number of extraction. These results agreed with the calculated results by geochemical modeling. Understanding the major chemical species of hazardous elements leached from mudstones is valuable in the mitigation of these potential sources of contamination.

1. INTRODUCTION

Groundwater contamination of arsenic (As) is a serious worldwide problem. The most well known and notorious examples of this kind of environmental and health concerns are those reported in Bangladesh and West Bengal, India, which is affecting as many as 70 million people (Das et al., 1996; Acharyya et al., 2000; Nickson et al., 2000; Dowling et al., 2002; Ahmed et al., 2004; Akai et al., 2004). In addition, As contaminations in the USA (Welch et al., 1988; Robertson, 1989; Peters et al., 1999; Kelley et al., 2005), Canada (Wang and Mulligan, 2006), Mexico (Armienta et al., 1997), Argentina (Bundschuh et al., 2004), Taiwan (Chen et al., 1994), Vietnam (Berg et al., 2001; Berg et al., 2007), Cambodia (Berg et al., 2007; Polizzotto et al., 2008), and other countries have been widely reported. Natural As contamination of the groundwater resulting from bedrock aquifers have also been reported, including the crystalline aquifer in central New Hamshire (Peter and Blum, 2003), Triassic sandstone aquifer in Bavaria (Heinrichs and Udluft, 1999), and Ordovician sandstone aquifer in Wisconsin (Schreiber et al., 2000). In Japan, hydrothermally altered regions are ubiquitously distributed. Thus, leaching of naturally occurring heavy metals and metalloids from hydrothermally altered rocks is a common environmental concern because these rocks have high contents of heavy metals like lead (Pb) and metalloids like As. Marine sedimentary rock is also widely distributed all over Japan, which contain metalloids, such as As, selenium (Se), and boron (B). These metalloids have high mobilities in the environment primarily due to their anionic or uncharged chemical forms. Leaching of hazardous elements like Pb and As from altered rocks had been investigated by batch and column experiments (Igarashi et al., 2008; Tabelin and Igarashi, 2009; Tabelin et al., 2010, Tabelin et al., 2012, Tatsuhara et al., 2012).
However, these previously published works did not evaluate the effects of the chemical forms of redox-sensitive elements like As and Se in their leaching behaviors and subsequent mobility in the environment. The major inorganic chemical form of dissolved As is either arsenite As(III) or arsenate As(V) while that of Se is either selenite Se(IV) or selenate Se(VI). All of these chemical forms are oxyanions. Therefore, it is of importance to clarify the chemical forms of As and Se released from hydrothermally altered rocks and sedimentary rocks like mudstones. Tabelin et al. (2012) pointed out that the leaching behaviors of As(III) and As(V) in column experiments were complicated. However, changes in the chemical forms of As leached from such rocks have never closely been examined. In addition, the chemical forms of Se leached from the rocks have never been reported before. Thus, the chemical forms of As and Se leached from rocks were elucidated in this study by simple and consecutive batch experiments.

2. MATERIALS AND METHODS

2.1. Rock Samples

Two mudstone samples were collected from different tunnel construction projects in the island of Hokkaido, Japan. The rock samples are from S tunnel (S sample) and O-tunnel (O sample). Both samples were formed during the Cretaceous period. The rock samples were air dried, crushed, sieved through a 2-mm-aperture screen, and stored in airtight containers.

For the chemical and mineralogical analyses, the samples were further crushed to less than 50 μm and then analyzed using an X-ray fluorescence spectrometer (SpectroXepos, Rigaku Corporation, Japan) and an X-ray diffractometer (MultiFlex, Rigaku Corporation, Japan), respectively. Selenium contents of the rock samples were determined using the wet method. The loss on ignition was measured based on the gravimetrical method.

The mineralogical properties of the samples are listed in Table 1. The major minerals are aluminosilicates, and pyrite was also detected in both samples. The chemical properties are shown in Table 2. The sulfur contents are 0.38 wt.% for S sample and 0.23 wt.% for O sample while the As contents are 10 mg/kg for S sample and 21 mg/kg for O sample. Selenium in the samples amounts to 0.6 and 0.4 mg/kg for S and O samples, respectively. The As and Se contents of these rocks are slightly higher than the background data.

2.2. Batch Leaching Experiments

Batch leaching experiments were conducted by mixing 15 or 30 g of crushed rock sample with 150 mL of deionized water (solid-liquid ratio = 1:5 or 1:10) at 120 rpm for 30 min, 2, 6, and 24 h. After the predetermined reaction time, the pH, electrical conductivity (EC) and oxidation-reduction potential (Eh) of the suspensions were measured and the leachates were filtered through 0.45 μm membrane filters for chemical analysis.

2.3. Consecutive Batch Leaching Experiments

Consecutive batch leaching experiments were conducted using 1:5 and 1:10 solid-liquid ratios. The suspensions were shaken at 120 rpm for 24 h. After shaking, the pH, EC, and Eh were measured followed by filtration of the suspension using a 0.45 μm membrane filter. The filtrates were collected for the chemical analysis while the residue was reused for the next extraction using the same solid-liquid ratio. These series of mixing and filtration steps were repeated six times. All the filtrates collected were provided for chemical analysis.

2.4. Chemical Analysis

Concentrations of As and Se were analyzed using a hydride generator attached to an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan). For the speciation of As, filtered and unacidified leachates were passed through WATERS Sep-Pak® Plus Acell Plus QMA cartridges (Waters, USA). These

<table>
<thead>
<tr>
<th>Table 1 Results of XRF analysis</th>
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<tr>
<td></td>
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<tr>
<td>Quartz</td>
</tr>
<tr>
<td>S sample</td>
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<td>O sample</td>
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*+++: Strong, ++ Medium, +: Weak, -: Trace
are solid phase extraction cartridges that are able to immobilize As(V) while allowing As(III) to pass through (Impellitteri, 2004; Al-Abed et al., 2006). The leachates passing through the QMA cartridges were collected and analyzed in terms of As(III). Arsenate was calculated from the total As and As(III) concentrations in the leachate. For the speciation of Se, the filtered samples were pretreated to reduce Se(VI) to Se(IV). After the pretreatments, the total Se concentrations (Se(IV) + Se(VI)) were obtained. Without pretreatments, only Se(IV) could be detected by the ICP-AES + hydride generator method. The major ions in the leachate were analyzed by ion chromatographs.

3. GEOCHEMICAL MODELING
Eh-pH diagrams of As and Se were constructed using the Geochemist’s Workbench (Bethke, 1992) based on the measured chemical properties of the leachates.

4. RESULTS AND DISCUSSION
4.1. Batch Leaching Experiments
The leaching behavior and chemical forms of As with time at the solid-liquid ratio of 1:10 are presented in Figure 1. The As concentrations increased with the mixing time and were higher than 10 μg/L after 6 hours for both samples. However, the As concentrations in the leachate of O sample were 10 times higher than those of S sample. The major chemical forms of As was As(V) for both samples. In particular, almost all of the As leached from O sample was As(V).

The leaching behavior and chemical forms of Se with time at the solid-liquid ratio of 1:5 are presented in Figure 2. The Se concentrations increased with the mixing time and were higher than 10 μg/L after 2 hours for both samples. The Se concentrations in the leachate of both samples approached 25 μg/L. The similar leaching concentrations of Se in both samples were different compared to those of As. The major chemical forms of Se was Se(VI) for both samples. Although the fraction of Se(IV) was relatively high at the beginning of the experiments, that of Se (VI) increased with mixing time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ (wt%)</th>
<th>TiO₂ (wt%)</th>
<th>Al₂O₃ (wt%)</th>
<th>Fe₂O₃ (wt%)</th>
<th>MnO (wt%)</th>
<th>MgO (wt%)</th>
<th>CaO (wt%)</th>
<th>Na₂O (wt%)</th>
<th>K₂O (wt%)</th>
<th>P₂O₅ (wt%)</th>
<th>S (wt%)</th>
<th>As (mg/kg)</th>
<th>Se (mg/kg)</th>
<th>LOI (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S sample</td>
<td>61.8</td>
<td>0.67</td>
<td>15.9</td>
<td>6.03</td>
<td>0.06</td>
<td>1.95</td>
<td>2.49</td>
<td>2.51</td>
<td>2.92</td>
<td>0.18</td>
<td>0.38</td>
<td>10.0</td>
<td>0.59</td>
<td>5.09</td>
</tr>
<tr>
<td>O sample</td>
<td>33.7</td>
<td>0.44</td>
<td>9.07</td>
<td>3.9</td>
<td>0.06</td>
<td>0.85</td>
<td>1.95</td>
<td>1.08</td>
<td>2.72</td>
<td>0.04</td>
<td>0.23</td>
<td>21.3</td>
<td>0.40</td>
<td>8.19</td>
</tr>
</tbody>
</table>
Figure 1 As concentration change with time in batch experiments (Solid-liquid ratio = 1:10).
Figure 2 Se concentration change with time in batch experiments (Solid-liquid ratio = 1:10).

4.2. Consecutive Batch Leaching Experiments

The leaching behavior and chemical forms of As with the number of extraction at the solid-liquid ratio of 1:5 are presented in Figure 3. The total As and As(V) concentrations in the leachate decreased with the number of extraction, and the major chemical form of As was As(V). However, small amounts of As(III) (< 10 μg/L) was observed independent of the number of extraction. This indicates that the leaching of As(III) continues whereas that of As(V) decreases. The total As concentrations at the 6th extraction were still higher than 10 μg/L for both samples. The leaching behavior and chemical forms of Se with the number of extraction at the solid-liquid ratio of 1:5 are shown in Figure 4. The total Se concentrations in the leachate decreased with the number of extraction, and after 2nd extraction, the total Se concentrations decreased below 10 μg/L. This indicates that the leachability or mobility of Se is higher than that of As. The major chemical form of Se changed from Se(VI) to Se(IV) with the number of extraction for S sample. However, the major chemical form of Se for O sample was Se(IV) irrespective of the number of extraction. The difference in the major chemical forms of Se in O and S samples might be attributed to the redox conditions of the leachates.
Figure 3 As concentration change with the number of extraction in consecutive batch experiments (Solid-liquid ratio = 1:5).

Figure 4 Se concentration change with the number of extraction in consecutive batch experiments (Solid-liquid ratio = 1:5).
4.3. Eh-pH Diagram
The Eh-pH diagrams of As and Se were drawn using the chemical data of the leachates as shown in Figs. 5 and 6, respectively. The measured data are also plotted in these figures. With respect to As, all of the plots are in the As(V)-dominant region. In contrast, the plots for Se are distributed around the boundary between Se(IV) and Se(VI). This indicates that the measured chemical forms of As and Se agrees with the calculated chemical forms in equilibrium. This means that the chemical forms of As and Se can be evaluated by equilibrium geochemical modeling.

5. CONCLUSION
The leaching behavior and chemical forms of As and Se leached from mudstone samples were evaluated by batch leaching experiments and geochemical modeling. The obtained results are as follows:

(1) Although the leaching concentrations of As and Se increased with mixing time in batch experiments, they decreased with the number of extraction in consecutive batch experiments.

(2) The major chemical form of As was As(V) regardless of the sample.

(3) The major chemical form of Se changed from Se(VI) to Se(IV) with the number of extraction.

(4) The measured major chemical forms of As and Se agreed with the calculated results using an equilibrium geochemical model.

Further researches are required to effectively immobilize As and Se leached from excavated rocks in the soil-groundwater environment based on their chemical forms.
REFERENCES


