Leaching characteristics of toxic elements from excavated altered rock and their release mechanisms

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Introduction
Recent tunnel projects in Japan for roads and other purposes have excavated rocks that had been hydrothermally altered. Because of this, the rocks contain elevated amounts of arsenic (As) and other toxic elements (e.g., lead (Pb), chromium (Cr), selenium (Se) and boron (B)), and are therefore potential sources of contamination. Arsenicosis, keratosis and cancers of the skin, kidney and lungs are some of the serious health problems associated with prolonged exposure to As contaminated soil and groundwater (O’Day et al., 2004; Sengupta, 2002). The most well known and notorious example of As contamination of groundwater are those reported in Bangladesh and West Bengal, India, which is affecting as much as 70 million people (Akai et al., 2004; Nickson et al., 2000). Aside from the well documented toxicity of As, it is especially problematic because of its high mobility under varying pH and redox conditions. Even at reducing conditions where other oxyanions like Cr and Se are already precipitated, As is still mobile because of the reductive dissolution of Fe-oxyhydroxides/oxides that have high As adsorption affinity and the reduction of As[V] to As[III] (Smedley and Kinniburgh, 2002). On the other hand, chronic Pb-poisoning causes paralysis of the peripheral motor nerves, anemia, kidney damage, abnormal fetal development and abnormal neurological development and function (Sengupta, 2002).

At the moment, special landfills are being used for the disposal of these hazardous waste rocks, but this is so expensive that new and alternative methods are being explored. Numerous studies have been reported about the hydrothermal alteration of rocks especially in the context of ore genesis, characterization and formation (Allen and Hahn, 1994; Huston et al., 1995), but studies regarding the leaching behavior and release mechanisms of As and Pb from altered rocks and the parameters that control these mechanisms are still lacking in the literature. Therefore, the main objective of this research is two-folds: first, to understand the leaching behavior and release mechanisms of As and Pb from altered rocks, and second, to develop an alternative disposal method for these rocks. Specifically, this study aims to achieve the following:

- Identify the main sources of As and Pb in altered rocks
- Elucidate the leaching behaviors of As and Pb under oxic, anoxic and reducing conditions using batch and column experiments
- Investigate the importance of pyrite and calcite on the mobilization of As and Pb from the rock
- Determine the speciation of As under oxic and anoxic condition using batch and column experiments
- Identify the main mechanisms controlling the mobilization and speciation of As from the altered rock with time and depth
- Develop a classification scheme to group excavated rocks with complex and variable chemical and mineralogical properties

Sources of arsenic and lead in the excavated rocks
Hydrothermal alteration enriches the rock samples with As and Pb preferentially in and around precipitated pyrite grains (Figure 1 and Table 1). The extent of enrichment generally depended on the chemical and physical properties of the hydrothermal solution responsible for the alteration, that is, a more mineralized solution resulted in higher amounts of As and Pb incorporated in the rock. Sources of As and Pb could also be grouped depending on their stabilities under varying geochemical conditions using sequential extraction. Using this method, we divided the sources of As and Pb into 5 phases: exchangeable, carbonates, Fe-Mn oxides, sulfides and organic matter, and residual/crystalline. Most of the As found in the altered rocks were associated with the sulfides and organics fraction while Pb was mostly incorporated in the residual/crystalline phase (Figures 2 and 3). Because of this, As is inherently more mobile than Pb in altered rocks. Significant concentrations of both As and Pb were also found in the exchangeable phase, which was most probably the result of the partial oxidation of pyrite found in the rock during excavation, transport and storage. Thus, pyrite is the primary source of As and Pb in altered rocks even if it is found only in trace amounts.
Factors affecting the mobilization of arsenic and lead from the rock

Among the important geochemical factors in the environment, we selected pH, Eh, O₂ and CO₂ and changed them in laboratory batch experiments. The leaching of As was highly pH dependent, that is, mobilization was enhanced under acidic and alkaline conditions with a minimum at circumneutral pH (Figure 2). Similarly, Pb leaching was also strongly dependent on the pH, but the amount released under alkaline conditions was lower relative to that of As (Figure 2). The release of these elements was also dependent on the Eh. Leaching of As was enhanced under both oxidizing and reducing conditions, but Pb was immobilized under reducing conditions in the entire pH range (Figure 3). Because O₂ is essential in pyrite oxidation, anoxic conditions minimized the release of both As and Pb. On the other hand, CO₂ did not directly affect the amount of As and Pb released from the rock, but it enhanced the dissolution of calcite and influenced the pH of the rock-water system. Based on these results, we deduced the mechanisms involved in the mobilization of As from the rock that included: acid and reductive dissolution, pyrite oxidation, precipitation and adsorption/desorption reactions depending on the pH, Eh, O₂ and CO₂ concentration.

Also, although excavated rocks have variable chemical and mineralogical properties, we have developed a classification based on the relative abundance of pyrite and calcite and their pH when in contact with water: pyritic/acidic and calcareous/alkaline.

### Table 1. EPMA data of As and Pb from minerals in the altered and unaltered zone of the sedimentary rock.

#### Altered zone

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>No.</th>
<th>S (wt%)</th>
<th>Fe (wt%)</th>
<th>As (wt%)</th>
<th>Pb (wt%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>1</td>
<td>49.8</td>
<td>46.2</td>
<td>0.13</td>
<td>&lt;0.01</td>
<td>96.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>49.5</td>
<td>45.3</td>
<td>0.11</td>
<td>&lt;0.01</td>
<td>94.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>50.5</td>
<td>43.3</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>93.9</td>
</tr>
<tr>
<td>Smectite</td>
<td>1</td>
<td>0.01</td>
<td>3.42</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>3.47</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.01</td>
<td>4.63</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>4.64</td>
</tr>
<tr>
<td>Illite</td>
<td>1</td>
<td>0.01</td>
<td>3.25</td>
<td>0.07</td>
<td>0.03</td>
<td>3.29</td>
</tr>
</tbody>
</table>

#### Unaltered zone

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>No.</th>
<th>S (wt%)</th>
<th>Fe (wt%)</th>
<th>As (wt%)</th>
<th>Pb (wt%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>1</td>
<td>50.9</td>
<td>46.7</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>97.6</td>
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<tr>
<td></td>
<td>2</td>
<td>51</td>
<td>46.1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>51.2</td>
<td>45.7</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>96.9</td>
</tr>
<tr>
<td>Calcite</td>
<td>1</td>
<td>0.06</td>
<td>0.22</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 1. The elemental maps of Fe (a), S (b), As (c), Si (d), and Al (e) from the altered volcanic rock at a magnification of 40 µm.

Figure 2. As and Pb concentrations in the leachate of altered volcanic rocks under anoxic conditions: As concentration as a function of pH (a) and Pb concentration as a function of pH (b).
Mobilization and speciation of arsenic in column experiments under oxic condition

The experimental design was expanded using columns under ambient conditions to understand the mobilization and speciation of As with variations in the infiltration rate, rock bed thickness and bulk density. These are the parameters that could be engineered during the actual disposal of the rock. Changes in these three parameters had the same effect on the release of As, which was attributed to the water residence time. Increasing the infiltration rate had the same effect on the water residence time as decreasing the rock bed thickness and the bulk density. However, the effect of water residence time on the release of As from the rock was indirect. It is the pH, O₂ and CO₂ that directly affected the mechanisms controlling the movement of As in the columns. Higher pH values resulted in higher concentrations of As in the effluent especially during the early stages of the experiment (Figures 4 and 5). The pH was a result of the combined effects of pyrite oxidation, calcite dissolution and precipitation of Fe-oxyhydroxides/oxides. The mobilization of As with time could be divided into two stages: short-term and long-term (Figure 4). In the short-term phase lasting for about 20 weeks, dissolution of Fe and As-bearing phases, pyrite oxidation and Fe-oxyhydroxides/oxides precipitation controlled the release of As from the rock. This phase was also characterized by large fluctuations in the pH and concentrations of coexisting ions like Ca²⁺ and SO₄²⁻. In the long-term phase, the pH and concentrations of As and coexisting ions stabilized. Because soluble Fe and As-bearing phases had been dissolved before this phase, the mechanisms of As release from the altered rock was due to the continued oxidation of pyrite in the presence of calcite. However, since pyrite oxidation released Fe ions, precipitation of Fe-oxyhydroxides/oxides that could act as As-adsorbents also occurred. Thus, the amount of As in the effluent is due to the combined effects of these processes. We understood that the columns were divided into a “leaching” and “adsorption” region. Leaching predominantly occurred at the upper half while adsorption happened at the bottom half of the columns. The existence of this “adsorption” region allowed the rock to attenuate additional As loadings spiked into the columns. Under ambient conditions, both As[V] and As[III] predominated in the effluent and was attributed to the pH-dependent adsorption of these species onto Fe-oxyhydroxides/oxides (Figure 6).

Figure 3. As and Pb concentrations in the leachate of altered volcanic rocks under oxic and reducing conditions: As concentration as a function of pH (a) and Pb concentration as a function of pH (b).

Figure 4. Effects of infiltration rate on the pH and As concentration; pH change with PV (a) and As concentration in the effluent with PV (b). Infiltration rates at quantities equivalent to 20, 40 and 80 mm/week of rainfall were added to cases 1, 2 and 3, respectively.
Mobilization and speciation of arsenic in column experiments under anoxic condition

Under anoxic conditions, the indirect effect of water residence time on the release of As became more pronounced (Figure 7). The effect of pH on the leaching of As was also similar to those observed under oxic conditions, that is, higher pH resulted in higher As concentrations in the effluent. Similarly, the mobilization of As with time could also be divided into a short-term and a long-term phase. Moreover, the mechanisms controlling the release of As from the altered rock were similar. However, the amounts of As released from the altered rock during the short-term phase under anoxic condition were significantly higher than those measured under oxic conditions. This was attributed to the reduction of Fe-oxyhydroxides/oxides precipitation in this phase where most of the soluble Fe and As-bearing minerals were dissolved. Both As[V] and As[III] species were also important under anoxic conditions. Arsenic[V] was the dominant species in the effluent during the initial and final stages of the experiments while As[III] predominated around the middle part of the experiment (Figure 8). The speciation of As was also due to pH-dependent adsorption of As species onto Fe-oxyhydroxide/oxides similar to that under oxic conditions.

Figure 5. Effects of rock bed thickness on the pH and As concentration; pH change with PV (a) and As concentration in the effluent with PV (b). Rock bed thicknesses of 100, 200 and 250 mm were used for cases 5, 2 and 6, respectively.

Figure 6. Evolution of total As, arsenate (As[V]) and arsenite (As[III]) concentrations with time in the effluent under oxic condition: Case 2 (a) and Case 3 (b).

Figure 7. Effects of infiltration rate on the pH and As concentration under anoxic conditions; pH change with PV (a) and As concentration in the effluent with PV (b).
Mobilization of arsenic under impoundment-type in situ experiments

In the field, the weather and temperature played an important role in the leaching of As because it directly affected the infiltration rate into the impoundment. When rain was available during the spring, summer and autumn months, As was continuously leached out from the rock, but during winter, water infiltration stopped resulting in the retardation of As release (Figures 9 and 10). Pyrite oxidation and adsorption onto Fe-oxyhydroxides/oxides and clay minerals were the primary mechanisms controlling the release of As during the in situ experiments (Figure 11). Also, the altered rock was capable of releasing As for a very long time because of the highly mobile nature of As and the continued oxidation of pyrite found in the rock.

Figure 8. Evolution of total As, arsenate (As[V]) and arsenite (As[III]) concentrations with time in the effluent under anoxic condition: Case 2 (a) and Case 3 (b).

Figure 9. Impoundments without covering soil (a) and with covering soil (b).

Figure 10. Changes in the As concentration of the pore water and the amount of rainfall with time (March 2006 – August 2007) at 0.5 m (a) and 1.5 m (b) of the impoundment of altered rock only.

Figure 11. Saturation indices of Fe and Al oxides, carbonates, clay minerals and calcium arsenate with time at a depth of 0.5 m for impoundment with rock only; Calcite[CaCO$_3$] ( ), Diaspore[AlO(OH)] ( ), Dolomite[CaMg(CO$_3$)$_2$] ( ), Fe(OH)$_3$ ( ), Goethite[FeOOH] ( ), Hematite[Fe$_2$O$_3$] ( ), Hydroxalite[Al$_2$O$_2$(OH)$_2$] ( ), Ca$_3$(AsO$_4$)$_2$.3H$_2$O ( ), Ca$_4$(OH)$_2$(AsO$_4$)$_2$.3H$_2$O ( ), Ca$_5$(AsO$_4$)$_3$.OH ( ) and CaHAsO$_4$.H$_2$O ( ).
The adsorption-layer system for the disposal of excavated rocks containing toxic elements

The best countermeasures to minimize the mobilization of As and Pb is to enhance and/or retard the mechanisms responsible for their release from the altered rock. Pyrite oxidation, which is the primary mechanism of As and Pb release from the altered rock could be minimized by reducing its exposure to the atmosphere. This could be done by using suitable low permeable soil covers. Immobilization of released As and Pb is also important in the disposal of the altered rock through the enhancement of adsorption and precipitation. This could be done using artificial and/or natural adsorbents. In both cases, the pH must be around circumneutral because precipitation and adsorption are highly favourable. Although excavated rocks also have variable chemical and mineralogical properties, we have devised a simple classification based on the relative abundance of pyrite and calcite and their pH when in contact with water: pyritic/acidic and calcareous/alkaline. This simple classification is essential in the disposal of these rocks because they have different properties and modes of As and Pb release. Pyritic/acidic rocks contain high amounts of pyrite with little or no calcite causing it to produce very acidic pH. In contrast, calcareous/alkaline rocks only contain trace amounts of pyrite and the acidic leachate produced by this mineral is readily neutralized by the abundant calcite. Taking all of these results into consideration, we are proposing the adsorption-layer system as an alternative disposal method for altered rocks. The name was based on the main immobilization mechanism of the system against toxic elements like As and Pb from the rock. This system is essentially composed of the following operations: enhancement of adsorption, reduction of infiltration and pH control. A conceptual diagram of this system is illustrated in Figure 12 and could be applied to both pyritic/acidic and calcareous/alkaline rocks with slight changes in the configuration.

References


Figure 12. The adsorption layer system