

## Change in the arsenic leaching from clayey soil by adding slag cement

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### Abstract

Cementitious materials are commonly used to reinforce the structural stability of clayey soils. However, there are very few data about the changes in arsenic (As) leaching from these soils due to the pH increase after the addition of cementitious materials to reinforce foundations. In this study, batch leaching tests were conducted using a clayey soil with different pH by changing the amount of addition of slag cement or the concentration of sodium hydroxide (NaOH). The results showed that the leaching concentration of As increased with increasing concentration of NaOH. However, when slag cement was added, the leaching concentration only increased at pH less than 10. At pH higher than 10, more slag cement addition translated to lower leaching concentration of As.

To understand the processes controlling the mobility of As in this system, we used a geochemical modeling software, PHREEQC, and the results suggest that As is adsorbed onto or coprecipitated with Fe-, Al-, Mg-, and/or Ca-bearing precipitates. By ultrafiltration, we found that these precipitates exist as colloidal particles at pH less than 10. Due to their minute sizes, however, these precipitates were rapidly dissolved at pH greater than 10 releasing As back into solution. Two Ca/Mg-based materials were also evaluated for their As sequestration capabilities. When added to the clayey soil-cement mixture, the concentration of As decreased indicating that these materials could be used to sequester dissolved As even under hyperalkaline pH conditions.

**Keywords:** arsenic, slag cement, leaching, pH, coexisting ions

### 1. Introduction

Cementitious materials are commonly used to reinforce clayey soils in many construction sites. For example, these materials are used in constructing embankments to prevent land subsidence. Cementitious materials are inherently alkaline, so when these are added to the clayey soils, the pH increases. Thus, arsenic (As) leaching is enhanced when clayey soils contain significant amount of this hazardous element.

Arsenic could exist in solution in both +3 (arsenite) and +5 (arsenate) oxidation states depending on redox conditions. The former is much more mobile than the latter because it could exist as an uncharged oxyanion at certain pH conditions. In contrast, arsenate is readily adsorbed onto positively charged surfaces because of it is usually present as a negatively charged arsenic oxyanion ( $\text{HAsO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ) in surface water and groundwater (Yoshimura and Akai, 2000). The surface of Fe-oxyhydroxides like goethite and hematite have

variable charges depending on the pH. These minerals have points of zero charge (PZC) around pH 7, so they exhibit positively charged surfaces at lower pH and negatively charged at higher pH. This is one of the reasons why As concentration has been observed to increase with increasing pH. Tabela and Igarashi (2009) showed that leaching concentration of As from hydrothermally altered rocks increased at alkaline pH. Moreover, Yoshimura and Akai (2000) proposed that As oxyanion is desorbed from the surface of iron hydroxide colloids with increasing pH, because of their variable charge.

Therefore, the effects of pH or addition of cement on As leaching from clayey soils were examined by batch leaching tests. In addition, the effectiveness of artificial materials to sequester As and reduce its leaching from these soils after cement addition was evaluated.

### 2. Materials and methods

## 2.1 Materials

Clayey soil was obtained from a boring core 14.5 to 16 m deep from a ground surface near Sapporo, Hokkaido, Japan. The soil is structurally weak and leaches As. The collected soil sample was air dried, lightly crushed using mortar and pestle, and sieved by a 2 mm aperture screen.

Blast furnace cement was selected as an additive to reinforce the clayey soil sample in this experiment because it could improve the structural stability of organic-rich soils.

Two different types of artificial materials were used to immobilize As in the leachate: Earth Tight (AT) (Nippon steel & Sumikin cement, Japan), and Add Rock Magnum (AM) (Okamoto Kogyo, Japan). The main component of both AT and AM are calcium and magnesium, respectively.

## 2.2 Batch leaching tests

Batch leaching tests were conducted under ambient conditions using a solid-liquid ratio of 1:10 and cement to soil mixing ratios ranging from 0.015 to 0.3 g cement/15 g soil. The pH, electrical conductivity (EC), oxidation-reduction potential (ORP) and temperature were measured after mixing at 200 rpm for 6 h. After centrifugation at 5,000 rpm for 40 to 70 minutes, the leachate was filtered through 0.45  $\mu\text{m}$  membrane filters. To compare the effects of competing cations, batch tests were conducted under the same conditions as above but with the addition of 1 to 20 mM NaOH solutions.

Furthermore, ultrafiltration using ultrafilter syringe units (Advantec, Japan) was used to evaluate the effects of colloidal particles, which were not removed by the 0.45  $\mu\text{m}$  membrane filters. Fifteen grams of clayey soil and 150 mL of deionized water were mixed with or without 0.15 g of cement. After

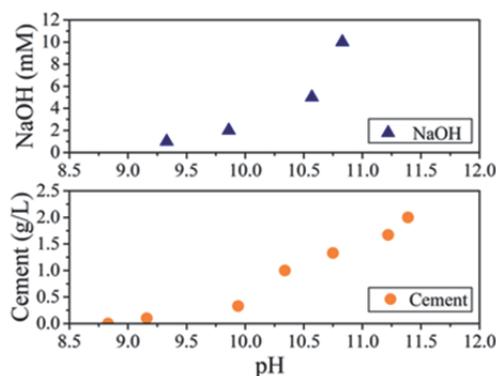


Fig. 1 NaOH concentration or the amount of cement added vs. pH.

mixing at 200 rpm for 6 h, pH, EC, ORP and temperature of the suspensions were measured. They were then centrifuged and filtered through 0.45  $\mu\text{m}$  membrane filters. After filtration, the filtrate was further filtered through ultrafilters with cut-off molecular weight of 200 kDa and 10 kDa.

## 2.3 Arsenic sequestration tests

Batch leaching tests to sequester As using AT and AM were conducted to understand how As leaching concentration was reduced. Fifteen grams of soil and 150 mL of deionized water were mixed with 0.05 and 0.1 g of AM or AT. Furthermore, 15 g of soil and 150 mL deionized water were mixed with 0.15 g of cement and 0.05 to 0.3 g of AM or AT. The leaching time was fixed at 6 h and the mixing speed at 200 rpm. After the pH, EC, ORP, and temperature of the suspensions were measured, the suspensions were centrifuged (5,000 rpm for 60 minutes), and filtered through 0.45  $\mu\text{m}$  membrane filters.

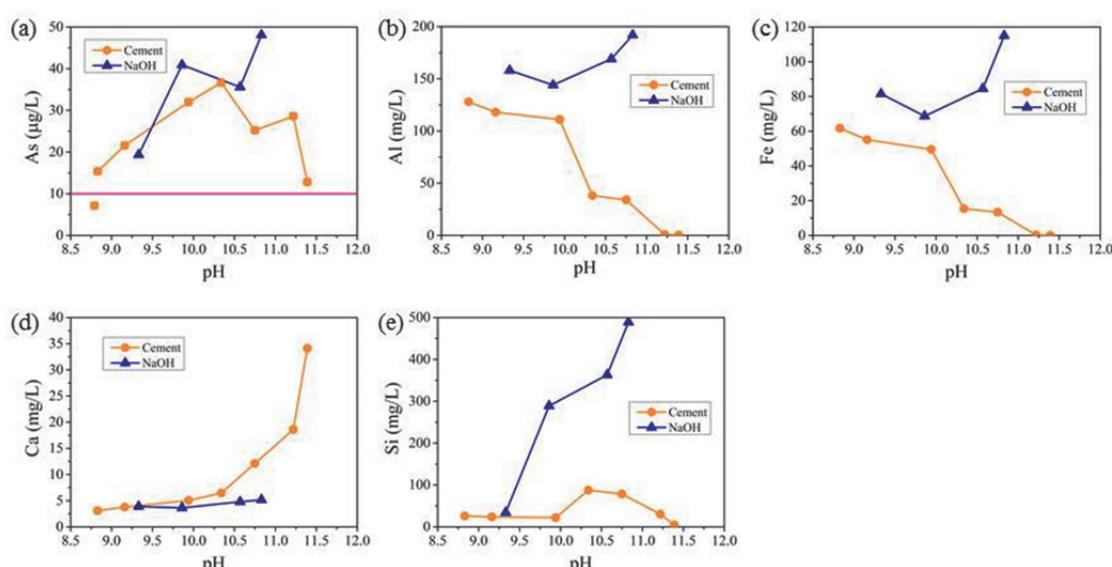


Fig. 2 Leaching concentrations of (a) arsenic, (b) aluminum, (c) iron, (d) calcium and (e) silica vs. pH.

## 2.4 Chemical analysis

Arsenic and other coexisting constituents, such as Na, Al, Fe, Mg, K, Ca, and Si were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Shimadzu Corporation, Japan). Chloride (Cl<sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) ions were measured by an anion chromatograph. Total organic carbon (TOC) was also measured by TOC-L (Shimadzu Corporation, Japan).

## 2.5 Calculation of saturation indices (SIs) of minerals

SIs and the speciation of coexisting constituents were calculated using a geochemical modeling software, PHREEQC (Parkhurst and Appelo, 1999).

## 3. Results and discussion

### 3.1 Batch tests

Figure 1 shows pH as a function of NaOH concentration or amount of added cement in batch leaching tests. The pH simply increased with NaOH concentration and the amount of added cement.

Figure 2 represents As and coexisting constituent concentration as a function of pH. The red line in Fig. 2 (a) represents the environmental standard of Japan for As. In all cases except one plot, leaching concentration of As exceeded the Japanese environmental standard.

When NaOH was used for pH adjustment, As concentration increased with pH. On the other hand, when cement was used, As concentration increased with the addition of the cement at pH less than 10, and then the leaching concentration decreased at pH higher than 10. These results indicate that As leached from

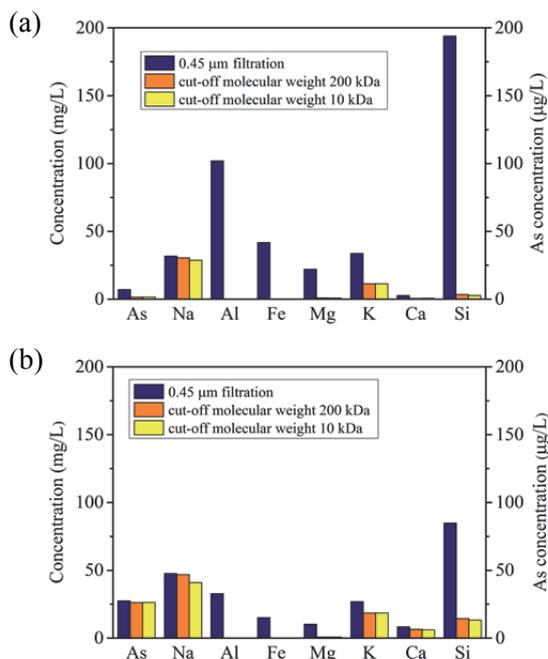


Fig. 3 Chemical properties of leachate (a) without cement, (b) with 0.15 g of cement.

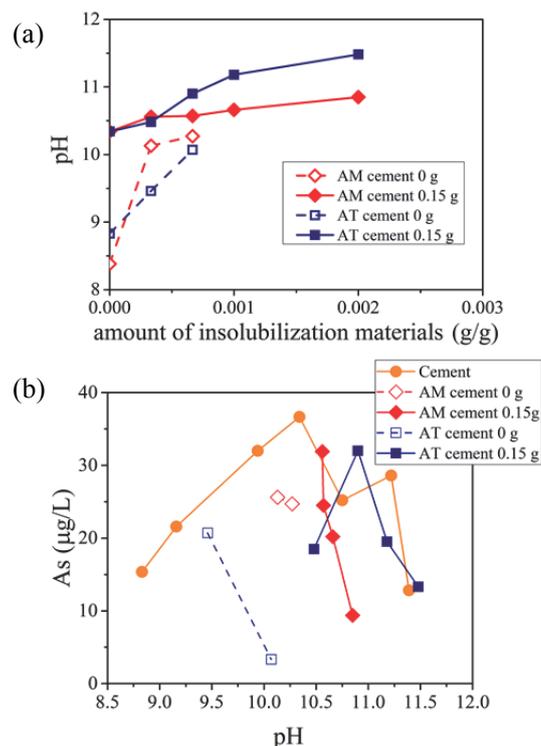


Fig. 4 (a) pH vs. the amount of added Ca/Mg-based materials and (b) As concentration vs. pH.

the soil depends not only on the pH but also on other coexisting constituents present in the leachate.

Aluminum and Fe concentrations decreased with cement addition. In particular, they decreased dramatically at pH higher than 10 (Figs. 2 (b) and (c)). Precipitations of Al- and Fe-bearing minerals were formed at higher pH because Ca concentration released from cement increased with pH (Fig. 2 (d)). Silica concentration also decreased with Ca concentration at higher pH (Fig. 2 (e)).

Concentrations of As and coexisting constituents using different filters are presented in Fig. 3. In the batch tests without cement, As concentration decreased from 7 µg/L to 2 µg/L by ultrafiltration at around pH 8.5. Similarly, concentrations of Al, Fe, Mg, and Si decreased to almost zero after 10 kDa ultrafiltration (Fig. 3 (a)). In contrast, As concentration did not decrease at pH 10.3 in the batch leaching tests with cement. However, the concentrations of Al, Fe, and Mg decreased to almost zero. These suggest that As is adsorbed onto colloidal particles of Al, Fe, Mg, and/or Si without cement while As is dissolved with cement.

### 3.2 Arsenic sequestration tests

Changes in pH of the leachate after the addition of AT and AM are shown in Fig. 4(a). The pH increased with increasing AT and AM addition and these changes were similar to those without cement. However, the pH became higher when AT was used compared to AM with cement. The pH of the leachate with cement was

higher than that without cement regardless of whether AT or AM was added.

Figure 4(b) shows the leaching concentration of As with and without AT or AM. Although As concentrations in almost all experiments decreased with increasing pH by adding these artificial materials, As concentration increased in some experiments after adding AT. This could be attributed to the lower pH and lower concentrations of Ca and/or Mg. This means that the effectiveness the artificial materials to sequester As depended on the pH.

### 3.3 Calculation of $SIs$ of minerals

Figure 5 shows  $SI$  as a function of pH. The  $SIs$  of gibbsite, boehmite,  $Al(OH)_3$ (amorphous(am)), and  $Fe(OH)_3$ (am) decreased with increasing pH when cement was added. Only the  $SI$  of  $Al(OH)_3$ (am) was changed from positive to negative at pH 9.7 whereas  $SIs$  of the other Al- and Fe-bearing minerals were positive irrespective of pH. It is well known that As is adsorbed onto  $Fe(OH)_3$  and  $Al(OH)_3$  (Masuda, 2000; Kaneko, 1981). These precipitates were dissolved with increasing pH.

On the contrary, the  $SIs$  of calcite and brucite increased with pH, and changed from negative to positive. These mean that the precipitates of Mg and/or Ca are related to As leaching concentration.

The  $SIs$  in cases with NaOH solution were similar

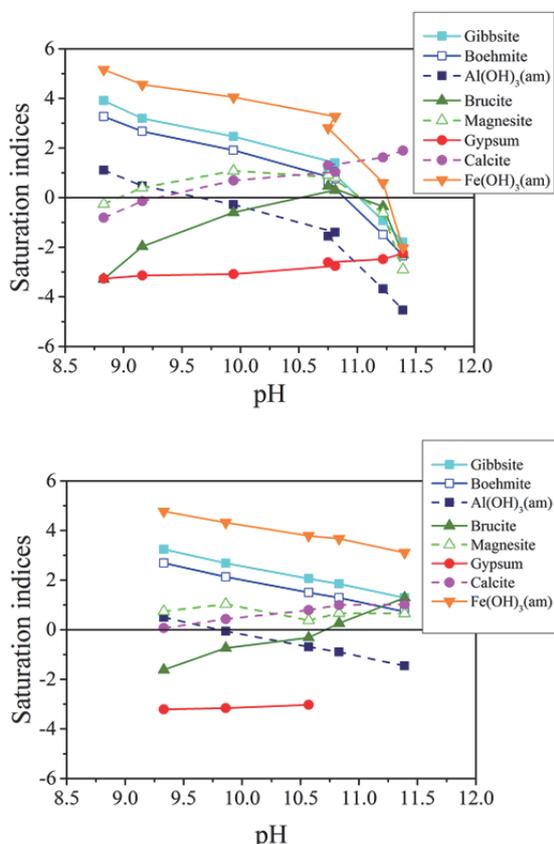


Fig. 5  $SIs$  vs. pH (a) with cement and (b) with NaOH.

to those of cement as shown in Fig. 5(a). The differences were the changes in  $SIs$  of brucite and gibbsite. These calculated results indicate that As may be adsorbed onto or coprecipitated with Al-, Mg-, and/or Ca-bearing minerals.

### 4. Conclusion

Arsenic concentration leached from a clayey soil containing As was increased with pH. When cement was used, the maximum leaching concentration of As was observed at pH 10.3. However, As concentration was lowered below  $10 \mu\text{g/L}$  even under the high pH condition by adding adequate amount of Ca and Mg-containing artificial materials most probably because of its adsorption and/or coprecipitation with Al-, Mg-, and/or Ca-bearing minerals.

### References

- Kaneko, E. (1981): Effect of silicic acid on the coprecipitation of arsenic with iron (III) hydroxide, *The Japan Society for Analytical Chemistry*, Vol. 30, No. 2, pp.117-122.
- Masuda, H. (2000) : Geochemical cycle of arsenic in the Earth's surface and mechanisms of its pollution of groundwater, *Journal of Groundwater Hydrology*, Vol. 42, No. 4, pp. 295-313.
- Parkhurst, D.L. and Appelo, C.A.J. (1999): User's guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. US Department of Interior and US Geol. Surv. Water-Resour. Invest. Rep. 99-4259.
- Tabelin, C. B. and Igarashi, T. (2009) : Mechanisms of arsenic and lead release from hydrothermally altered rock, *Journal of Hazardous Materials*, Vol. 169, pp. 980-990.
- Yoshimura, T. and Akai, J. (2000): Arsenic behavior in soils and sediments, and groundwater pollution: A review, *Earth Science*, Vol. 57, pp. 137-154.