Memoirs of the Faculty of Engineering, Kyushu University, Vol.68, No.2, June 2008

# Influence of Redox Potential on Arsenic Release from Soil in the Presence of Iron Oxyhydroxide

by

Kim Phuong NGUYEN[†], Ryuichi ITOI[*] and Rie YAMASHIRO[**]

(Received May 15, 2008)


## Abstract

This paper presents the effects redox potential on the mobility of arsenic (As) from soil in the presence of iron oxyhydroxide with soil column experiment. The mineralogical characteristics of the soil were identified by acid digestion, X-ray diffraction and sequential extraction methods. Approximately 60% of the total arsenic was associated with iron oxyhydroxides and iron oxides. Redox potential played a significant role on the onset of arsenic and iron release from the soil. The arsenic and iron concentration of the effluent from the soil column suggested that the release of arsenic was related to reductive dissolution of Fe-oxyhydroxides. Results of soil column experiment also imply that arsenic remains being adsorbed to iron oxyhydroxide until its surface area becomes small because of transformation into more stabilized form.


**Keywords**: Arsenic, Sequential extraction, Redox potential, Reductive dissolution of iron oxyhydroxides

## 1. Introduction

The transport of arsenic from soil to groundwater and vice versa is dependent on soil–water interaction in the subsurface environment. Oxidation/reduction state in soil layer is a controlling chemical factor for arsenic transportation. Redox conditions in soil layers vary widely from +500 mV (surface soils) to −300 mV (strongly reducing conditions) [1)]. Iron oxides, clay minerals, and organic materials in soil will adsorb or desorb arsenic when the ionic composition and/or Eh–pH in soil water changes[2)]. Iron oxides existing as nodules and concretions are excellent scavengers for arsenic and are affected by changes in Eh and pH[3)]. Under oxidizing conditions, Fe(III) predominates and is primarily sequestered in soluble ferric hydroxide phases. Burial, flooding, or transport of organic material or other reducing agents into soil can initiate reduction condition and

[†] Graduate Student, Department of Earth Resources Engineering
[*] Professor, Department of Earth Resources Engineering
[**] Technical Assistant, Department of Earth Resources Engineering

subsequently lead to dissolution of ferric hydroxides[4]. The reductive dissolution of iron hydroxides can release ferrous iron into the pore water and leads to the precipitation of secondary minerals.

A wide variety of column experiments which address the role of pH and complexation are reported in the literature but very few have focused on the effect of changes in the redox potential (ORP) on contaminant release[5]. Contaminant release can be affected by either direct reduction or indirect effects such as precipitation of metal sulfides (e.g., CuS, $FeS_2$, MnS, ZnS) or dissolution of hydrous aluminum, iron and manganese oxides, releasing adsorbed or co-precipitated metals[4), 6), 7)]. Therefore, evaluation on mobility of contaminants such as arsenic using experimentally controlled reducing conditions will contribute to a better understanding of the geochemical and biological oxidation/reduction processes that affect arsenic transport in the subsurface environment. In the laboratory, reducing conditions may be realized by biological methods or the use of reducing chemical agents. Biological methods consist of batch incubation of the soil under flooded conditions to promote the specific activity of either indigenous or cultured anaerobic microorganisms[8]. These methods can take up to several weeks and are largely dependent upon the characteristics of the microorganisms and nutrients present in the soil. In contrast, the use of reducing chemical agents can easily control reducing conditions with specified degree of the condition.

In this study, the effect of redox potential on arsenic release from soil in the presence of iron oxyhydroxide was investigated. Chemical characterization of the soil was performed using sequential extraction (SE) procedures tha determine the chemical speciation of arsenic and iron. The ability of chemical reducing agents to produce different redox environments and impact of oxidizing/reducing conditions on the mobility of arsenic from soil in the presence of iron oxyhydroxide was also evaluated.

## 2. Methodology

### 2.1 Soil sample

Soil samples were collected in Sasaguri town, Kasuya Province, Fukuoka Prefecture, Japan (**Fig. 1**) and were examined for arsenic in soil solid phase by SE. Collected soils was also used for column experiment. Surface soil sample (0-10cm depth) was collected in the area where metamorphic rocks such as schist cover, being rich in magnesium and iron. The soil samples were brought into the laboratory, air-dried, disaggregated by manual crushing, homogenized, sieved retaining the < 2mm fraction and stored in airtight polyethylene bags until use for chemical analysis.

### 2.2 Soil characterization and chemical analysis

Soil pH was measured in soil:water (1:1) suspension after 1h of equilibration using a pH electrode (HORIBA D-54). Mineralogy was determined by XRD (Rigaku RINT 2100) analysis. Arsenic was analyzed by HG-AAS after digestion with strong acid mixture and 2ml $KMnO_4$ solution (2%) as follows:

- 1.0 g of sample was placed in a teflon beaker.
- 3ml of 0.1M HCl, 5ml of conc. $HNO_3$, 25ml conc. HF and 2ml $KMnO_4$ solution (2%) were added.
- The solution was heated about 150 - 180°C on a hot plate for 2 days. If necessary, the $KMnO_4$ solution (2%) was added to maintain the indicator color.
- Then evaporate the solution at about 250°C until nearly dry.

- The residue was dissolved with 5ml of 6M HCl and transferred to volumetric flask and made up to desired volume with deionized water.
- The digest was then filtered through 0.45 μm membrane filter to analyze total arsenic with HG-AAS.

Dissolved manganese and iron were qualitatively detected by inductively coupled plasma – atomic emission spectrometry (ICP-AES) (Vista-MPX) for the sample decomposed by use the same strong acid mixture. Inorganic arsenic was volatized as arsine with sodium borohydride-hydrochloric acid solution using hydride generation equipment then analyzed with the HG-AAS (SOLAAR S4 with detection limit 1μg/l).

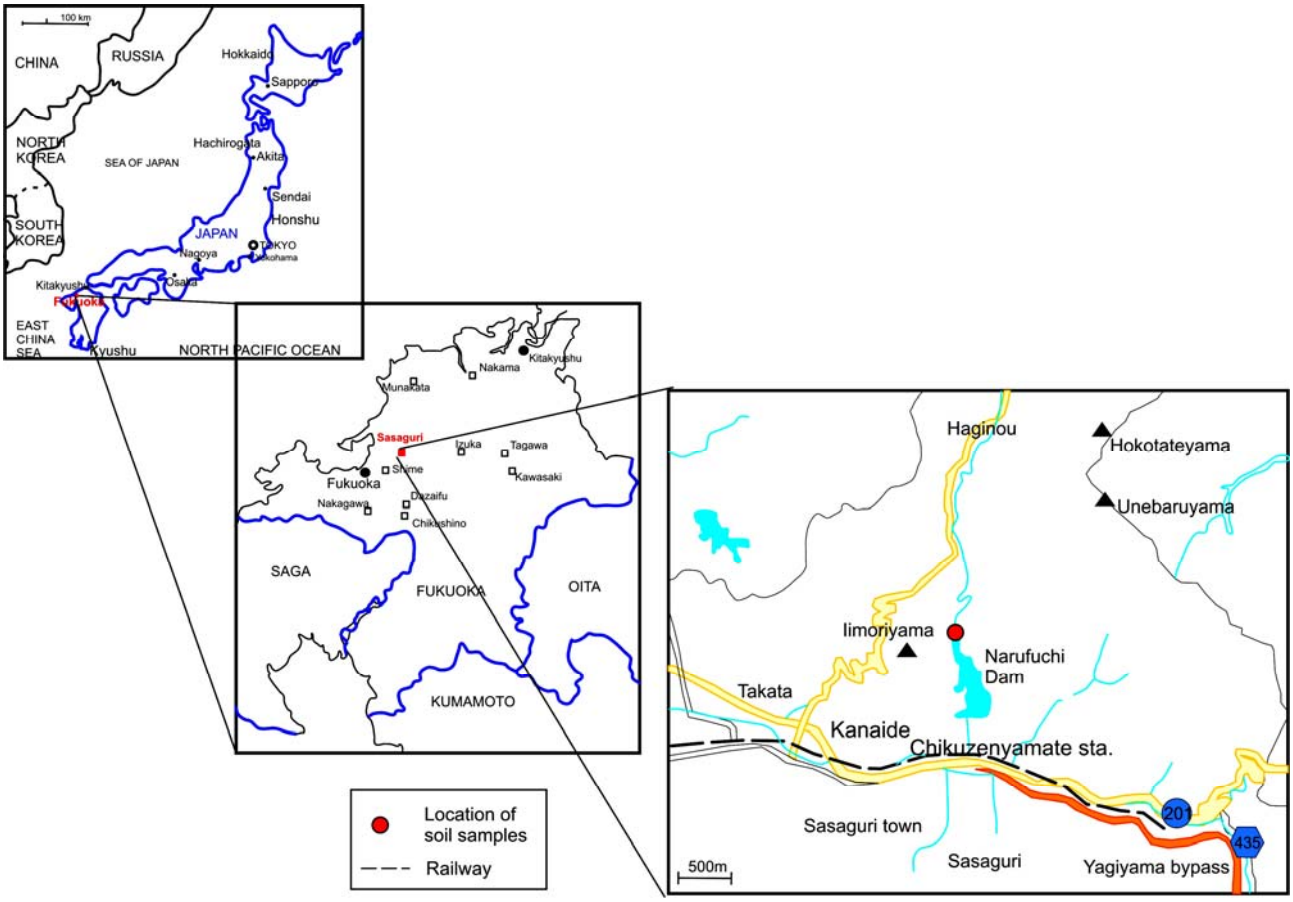



**Fig. 1** Location of soil samples in Sasaguri, Fukuoka Prefecture, Japan.

### 2.3 Sequential extraction procedure

**Figure 2** shows flowchart of the sequential extraction method by Tessier et al[9]. The first fraction provides As components that can be extracted as exchangeable ion. This extraction step consists of weighing 1 g of soils into 50ml centrifugation tubes and adding 25ml of 1M $CH_3COONH_4$ at pH of 7. The mixture was shaked with a shaker for 1 h at room temperature (**Fig. 2**). After shaking the tube containing the mixture were centrifuged for 20 min at 4500rpm. The supernatant was decanted and filtered through 0.45μm membrane filter. Then the remaining residue was rinsed with 10ml distilled and deionized water and the rinsate was discarded. This procedure

was repeated until the last extraction step (**Fig. 2**). It was recommended by Keon et al[10] to wash extractant after each step in order to remove any potentially readsorbed arsenic.

All the filtrates collected were acidified with HCl prior to analysis for arsenic with HG-AAS and iron, aluminum, manganese contents with ICP-AES. The accuracy of the result of sequential extraction was evaluated by comparing the sum of the five fractions with a single digestion by strong acid mixture using linear regression and correlation analysis.

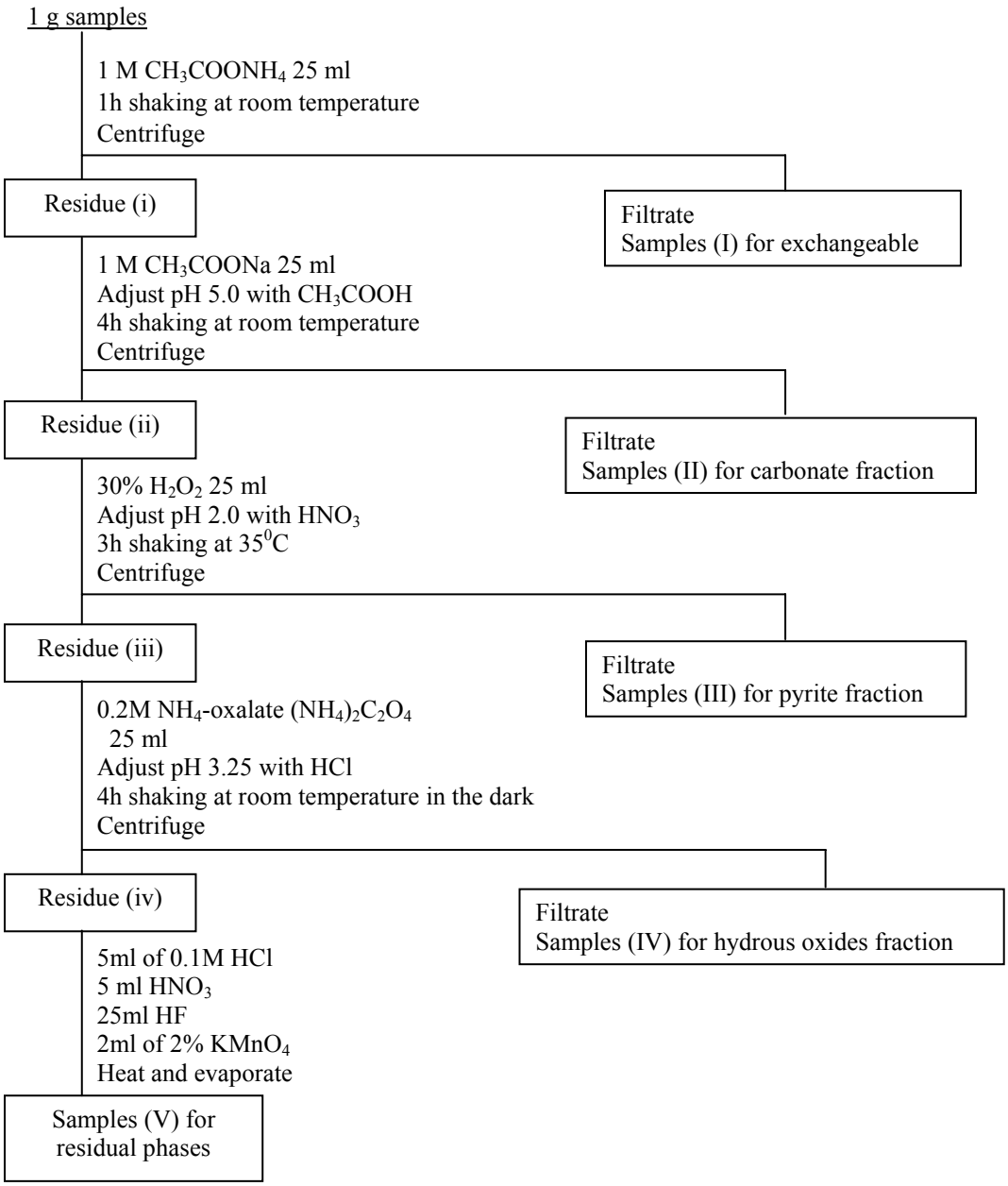



**Fig. 2** Flowchart of sequential extraction method.

### 2.4 Soil column experiment under controlled pH and redox conditions

#### 2.4.1 Experimental set up

A schematic experimental set up is shown in **Fig. 3**. The apparatus consists of cylindrical cell, storage tank of solution, pump, over flow tank and manometers. The soil column was made by packing mixture of soil and coprecipitate in the cell. The cell is 50 cm long and 8 cm across. Soil was packed in the cell of 34 cm long with 5 cm layers of ceramic beads of 2 mm diameter both top and bottom of the soil column. The soil column characteristics are shown in **Table 1**. Filter paper was placed at the bottom of the column to avoid soil particle flowing out. The cell was set in a vertical position, and tap water was first supplied from the bottom to fill pore space of the soil column.

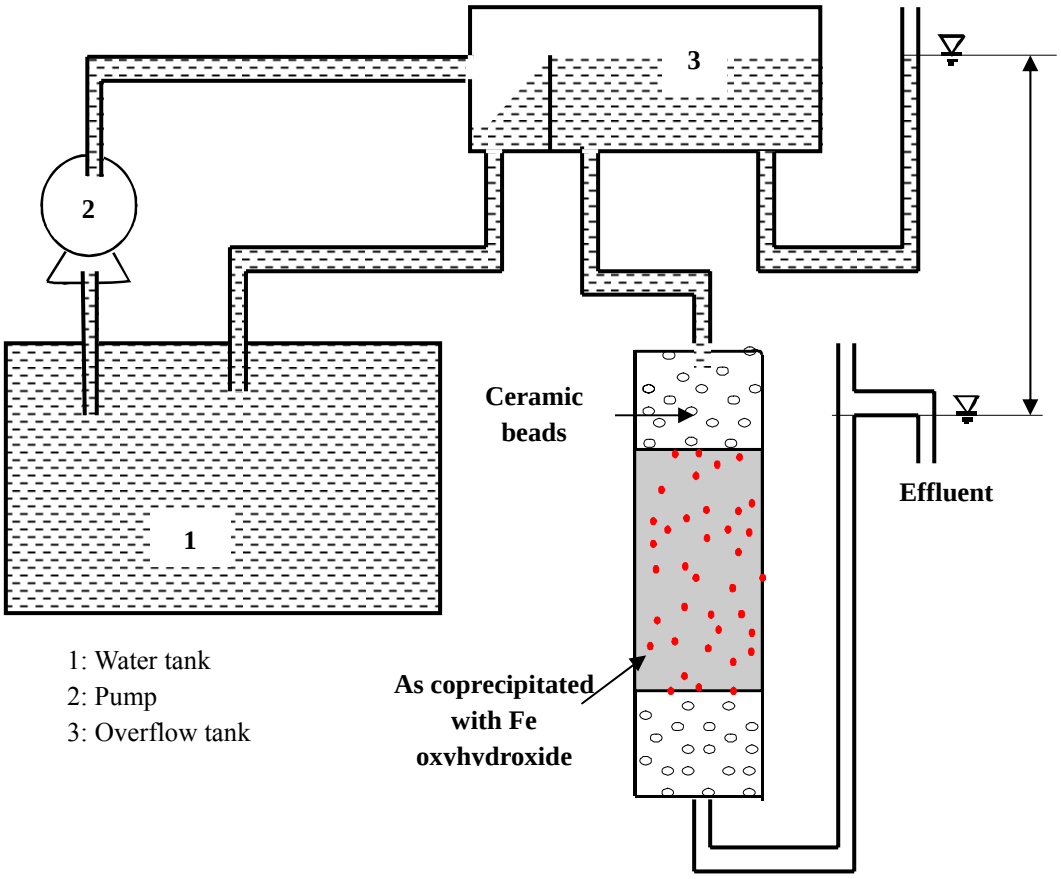



**Fig. 3** Schematic diagram of the soil column experimental apparatus.

**Table 1** Column characteristics for the continuous-down flow experiment.

| Parameter | Soil column |
|---|---|
| Height | 34 cm |
| Diameter | 8 cm |
| Volume | 1709 $cm^3$ |
| Porosity | 43 % |
| Flow rate | 1.0 ml/min |
| Hydraulic Conductivity | 0.12 cm/min |

After the column was filled with the tap water, then the solution was fed from the top of the column under the constant head difference between the inlet and outlet of the column. The flow rate was kept constant at 1.0 ml/min during the experiment. In order to control the redox conditions of solution, tap water and ascorbate solution was supplied with a specified time interval. Effluents were sampled at intervals of 2 to 3 hours, and filtered by membrane filters (0.45μm) for the major constituents as a function of time. pH and ORP were measured immediately upon collection by a glass electrode and platinum combination electrode, respectively.

The main characteristics of the influents are such that tap water has pH 6.25 and ORP valued of 157 mV whereas ascorbate solution has pH 6.25 and ORP valued of -186 mV. The experiment was conducted under controlled redox and pH conditions by alternately supplying sodium ascorbate solution and tap water to perform reducing and oxidizing conditions in the column, respectively.

### 2.4.2 Preparation of coprecipitate packed for soil column

The column was packed with 1.6 kg soil mixed with 800g iron oxyhydroxide coprecipitated with arsenic (2:1). Iron oxyhydroxide coprecipitated with arsenic was prepared in the laboratory. A solution containing 475ml of 1M $FeCl_3$, 15ml of 1M $Na_2HAsO_4$. $7H_2O$ and 10 ml of 3M NaCl was placed in a 1L beaker and then adjusting the pH to 6.5 by adding 5M NaOH solution while stirring the mixture with a magnetic stirrer. The suspension was allowed to stabilize for 2h, during which time the pH was adjusted to maintain a value of 6.5. Then the suspension was filtered and filtered solid was washed with distilled water to remove dissolved salts. Iron oxyhydroxide coprecipitated with arsenic was air-dried and stored in dark before use.

## 3. Results

### 3.1 Characteristics of the soil

**Table 2** presents the total metal concentrations of the Sasaguri soil. The soil has high contents of iron (Fe, 230 g/kg soil), silion (Si, 330 g/kg soil , sulfur (S, 4.77 g/kg soil) were observed. Relatively high concentration of arsenic (As, 0.28 g/kg) and manganese (Mn, 0.65 g/kg) was also identified.

**Table 2** Characteristics of the Sasaguri soil.

| | |
|---|---|
| *Physical characteristics* | |
| Soil pH | 7.3 |
| Total carbon (wt%) | 1.58 |
| | |
| *Total concentration of elements (mg/kg soil)* | |
| Total arsenic | 27 |
| Iron | 210000 |
| Manganese | 65000 |
| Sulfur | 4770 |
| Silicon | 330000 |

**Figure 4** shows XRD pattern which consists of a plot of intensities (count per second) versus a detector angle 2θ (degree). Peaks correspond to the d-spacings of the strongest lines of minerals. XRD pattern shows the presence of goethite, magnetite and quartz as the predominant crystalline minarels (**Fig. 4**). No pyrites ($FeS_2$) or any other arsenic mineral such as arsenopyrite (FeAsS) or scorodite ($FeAsO_4$) were detected. This implies that arsenic presents in soil to be associated mostly with the crystalline iron (hydro)oxide phases or as residual sulfides.

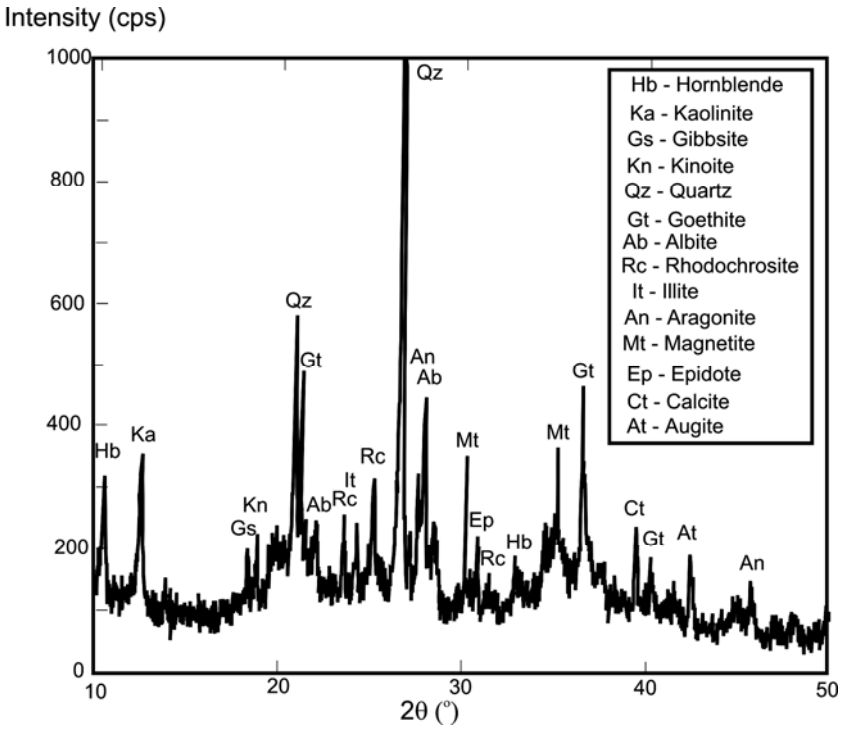



**Fig. 4** XRD pattern of Sasaguri soil sample.

### 3.2 Arsenic speciation in the soil

**Table 3** summarizes the analysis results of the sequential extraction method on the Sasaguri soil. The results indicate that arsenic of 1.86 mg/kg soil being equivalent to 7.2% of total arsenic present as exchangeable ion, while 2.09mg/kg soil (8%) and 0.9mg/kg soil (3.5%) are bound to carbonates and sulfide minerals, respectively. About 60% of the total arsenic (15.5 mg/kg soil) is associated with the amorphous and poorly crystalline iron oxides, and 22% with crystalline iron oxides or as residual materials (silicates or organic material). The results of sequential extraction on iron 138.6 g/kg soil and 48.08 g/kg soil present as crystalline oxides and residuals, respectively. The presence of amorphous and crystalline iron oxides and arsenic association with them indicates sorption or coprecipitation as the major mechanism for arsenic trappings in the soil. Strong arsenic association with $Fe_2O_3$ is known to occur due to the stabilization and transformation of thermodynamically unstable amorphous iron oxide to either goethite or hematite[11), 12)].

**Table 3** Results of sequential extraction method on the soil sample.

| Extraction step | As (mg/kg soil) | Fe (g/kg soil) |
|---|---|---|
| Exchangeable | 1.86 | 5.12 |
| $HCO_3$ fraction | 2.09 | 5.27 |
| Sulfide fraction | 0.90 | 7.05 |
| Amorphous and poorly crystalline Fe-Mn hydroxides | 15.47 | 138.60 |
| Residual phases | 5.68 | 48.08 |

### 3.3 Release of arsenic as effect of redox potential

**Figure 5** presents changes in pH and ORP values of effluents from the soil column with time. The results are indicated for three periods of column operation demarcated by different influent composition. For Period I and III, sodium ascorbate solution was supplied for providing reducing condition in the column. Period II presents that tap water was supplied for realizing oxidizing condition. Firstly, ascorbate solution was fed for 45 hours. Influent, then, was changed to tap water and fed for 100 hours followed by another supply of ascorbate solution for 60 hours.

Redox values remain negative and the same for 30 hours after the influent changed the influent then rapidly increase with time. This implies that oxidizing condition is eventually formed in the column after changing the influent to tap water. Redox values turn to positive at about 95 hours since the start of the experiment. ORP values then gradually increase and reach to the maximum value, +135mV, at about 142 hours. Then it remains the same value until 147 hours. Influent was changed to ascorbate solution at 142 hours to repeat redox condition in the column. ORP values start decrease soon after the influent changed from tap water to ascorbate solution, and shows continuous decrease down to -135 mV at about 202 hours. This implies that feeding sodium ascorbate solution leads to reducing condition throughout the column. A significant decrease in ORP from -143 mV to -229 mV (Period I) and from 135 mV to -135 mV (Period III) was observed. The largest change in ORP is observed from negative to positive values when the influent was changed from ascorbate solution to tap water. Redox potential of the column gradually changes from strongly-moderately reducing condition (-213 mV to -37 mV) to moderately oxidizing condition (-6 mV to 101 mV) in Period II. During experiment, pH gradually increases from 6.5 to 7.94.

Concentrations of arsenic and iron with ORP values of the effluent are shown in **Fig. 6(a)** and **6(b)**. There is an apparent relationship between arsenic and ORP values such that arsenic is detected only under condition of negative ORP values theirs concentrations seem to be correlated to the magnitude of ORP values. From **Fig 6(a)**, ORP values starts decreasing after 7 hours of commencement of supplying influent whereas arsenic and iron concentrations increase gradually up to 70 hours. For arsenic concentration, it reaches the highest concentration of 71.2 mg/L at 70 hours, then start decreasing which corresponds to an increase in ORP values.

On the other hand, iron concentrations increase with time in Period I and reach the highest concentration of 4154 mg/L at 20 hours. Then, its concentration starts decreasing whereas ORP value continue decreasing and remain negative (**Fig. 6(b)**). It can said that both arsenic and iron start decreasing once it reaches the maximum value, but iron concentration starts decreasing much faster than that of arsenic. At the beginning of period II, reducing condition remains in the column and arsenic concentration still increases. However, neither arsenic nor iron is detected when column is completely in oxidizing condition (**Fig. 6**). For addition of sodium ascorbate in period III that yield significant decrease in the ORP again, the increase in arsenic and iron concentration

seems to be indicative of a reductive dissolution of iron hydroxides. The release of iron accompanies by a simultaneous release of precipitated arsenic.

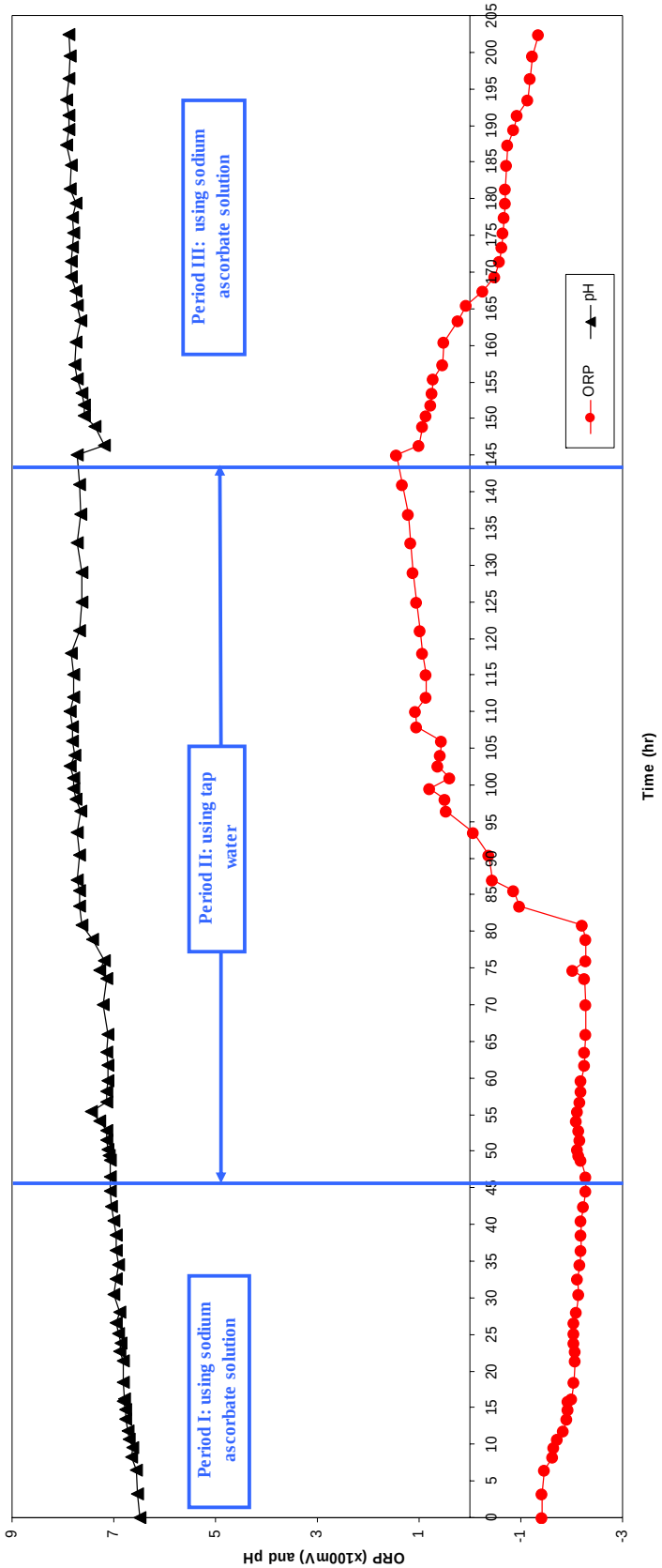
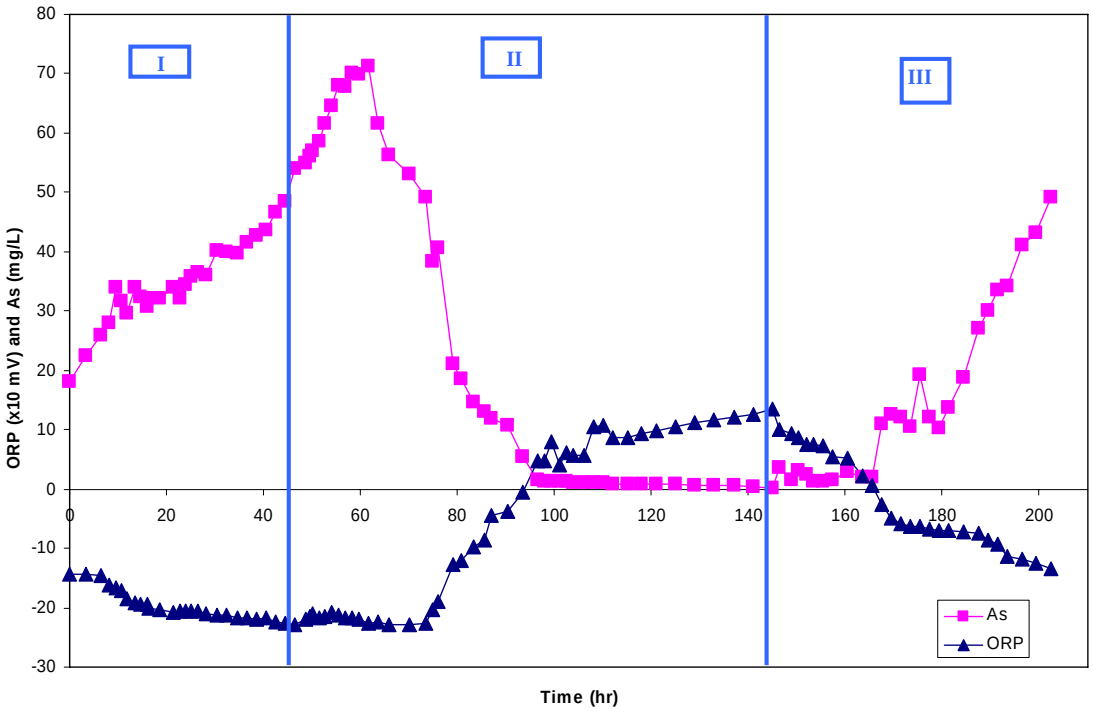



**Fig.5** Changes of ORP, pH of effluent with time.

( a )




( b )

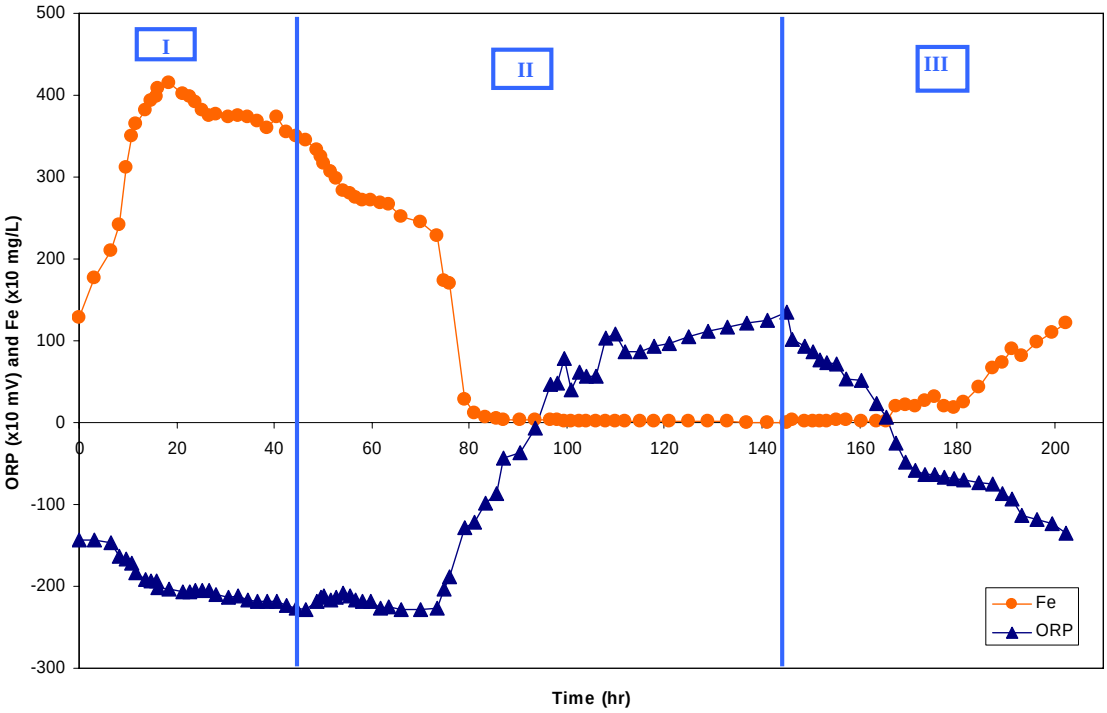



**Fig. 6** Relationship of ORP with concentration of (a) arsenic and (b) iron.

## 4. Discussions

### 4.1 Release of arsenic during reductive dissolution of iron oxyhydroxide

The release of arsenic coprecipitated with iron oxyhydroxide during reductive dissolution, was investigated using sodium ascorbate solution at pH 6.5-8. **Figure 7** shows pictures of the column taken at different elapsed time of the experiment. Increases iron concentrations in effluent correspond to change in color in the column from orange to black in the soil column. For example, changes in the color of the soil column reach 3cm and 24cm depth after 4h and 18h, respectively (**Fig. 7(a), (b)**). After 29h, there was little visible change (**Fig. 7(c)**). Results of iron concentrations from the column imply reductive dissolution of iron oxyhydroxide occurs, following by transport of dissolved iron and precipitation of secondary iron minerals.

Reductive dissolution of iron oxyhydroxide occurrs with an increase in total aqueous iron and arsenic. However, the release of arsenic from iron oxyhydroxide is significantly delayed compared to the release of iron (**Fig. 6(a), (b)**). Apparently, the dissolution of the ferric oxyhydroxide led to an increase in arsenic concentrations. The explanation is that partial dissolution of iron oxyhydroxide as the redox potential decreases may change concentration of iron and arsenic. However the arsenic remains being adsorbed on the surface of iron oxyhydroxide. During a rapid reductive dissolution of iron oxyhydroxide, elevated iron concentrations in porewater stimulate the transformation of iron oxyhydroxide to more stable crystalline forms whose surface area and the number of sites for arsenic being adsorbed become small to contain all the arsenic.

( a ) ( b ) ( c )

**Fig. 7** Pictures of the soil column during the experiment for different elapsed time. (a) 4h; (b) 18h and (c) 29h.

## 5. Conclusions

Characterization of the soil with sequential extraction method and XRD indicated the predominant presence of iron hydroxides either in crystalline form of goethite and hematite or in the amorphous form of iron oxyhydroxides which adsorbed or contained arsenic. Results of column experiment conducted under controlled pH and redox conditions indicated a strong dependence of

redox potential on both concentrations of arsenic and iron in effluents of the column. When the column was in moderately oxidizing conditions, As mainly associated with adsorption or co-precipitated onto Fe oxyhydroxides. Upon reduction, As mobilization increased significantly and was maximum. When the column was in highly reduced conditions in the column, As solubility seems to be controlled by the dissolution of Fe oxyhydroxides.

## Acknowledgements

The authors would like to thank Prof. Takushi Yokohama for many helpful discussions.

## References

1) A. S. Pastor, F. Burlo, et al.; Arsenic biochemistry as affected by phosphorus fertilizer addition, redox potential and pH in a west Bengal (India) soil, Geoderma, Vol. 137, pp. 504-510 (2007).
2) R. P. Gambrell, R.A. Khalid, et al.; Chemical availability of mercury, lead and zinc in Mobile Bay sediment suspension as affected by pH and oxidation–reduction conditions, Environ. Sci. Technol, Vol. 14, pp. 431–436 (1980).
3) T.C. Feijtel, R. D. DeLaune, et al.; Biogeochemical control on metal distribution and accumulation in Louisiana sediments, J. Environmental Quality, Vol. 17, pp. 88–94 (1988).
4) W. Stumm, B. Sulzberger; The cycling of iron in natural environments: considerations based on laboratory studies of heterogeneous redox processes, Geochim. Cosmochim. Acta, Vol. 56, pp. 3233–3257 (1992).
5) V. Chatain, F. Sanchez, et al.; Effect of experimentally induced reducing conditions on the mobility of arsenic from mining soil; Journal of Hazadous Materials, B122, pp. 119-128 (2005).
6) M. C. Chuan, G. Y. Shu, G. Y., et al.; Solubility of heavy metals in a contaminated soil: effects of redox potential and pH, Water Air Soil Pollut. Vol. 90, pp. 543–556 (1996).
7) M. Davranche, J. C. Bollinger; Heavy metals desorption from synthesized and natural iron and manganese oxyhydroxides: effect of reductive conditions, J. Colloid Interface Sci. Vol. 227, pp. 531–539 (2000).
8) C. J. Tadanier, M. E. Schreiber, et al.; Arsenic mobilization through microbial mediated deflocculation of Fe oxyhydroxide, Environ. Sci. Technol. Vol. 39, pp. 3061-3068 (2005).
9) A. Tessier, P. C. G. Campbell, et al.; Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. Vol. 51, pp. 844-851 (1979).
10) N. E. Keon, C. H. Swartz, et al.; Validation of an arsenic sequential extraction method for evaluating mobility in sediments, Environ. Sci. Technol. Vol. 35, pp. 2778-2784 (2001).
11) M. L. Pierce, C. B. Moore; Adsorption of arsenite and arsenate on amorphous iron hydroxides, Water Research, Vol.16, pp.1247-1353 (1982).
12) P. H. Masscheleyn, R. D. DeLaune, et al.; Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil, Environ. Sci. Technol. Vol. 25, pp. 1414–1419 (1991).