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メタデータ	言語: en 出版者: University of Miyazaki, IRISH 公開日: 2020-06-21 キーワード (Ja): キーワード (En): 作成者: 所, 千晴, 原口, 大輔, 井澤, 彩, Tokoro, Chiharu, Haraguchi, Daisuke, Izawa, Sayaka メールアドレス: 所属:
URL	http://hdl.handle.net/10458/5174

Sorption mechanism of As(V) co-precipitation with ferric or aluminum hydroxide in solution

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Abstract

Dilute arsenate (As(V)) coprecipitation by ferrihydrite or aluminum hydroxide was investigated to determine toward an efficient wastewater treatment. Coprecipitation experiment and simple adsorption one were exactly separated and five kinds of experimental investigation were conducted for both experiments, respectively; isotherm formation, zeta potential measurement, XRD analysis, FT-IR analysis and XAFS analysis. For both ferrihydrite and aluminum hydroxide, higher sorption densities were observed in coprecipitation experiments compared to adsorption experiments at pH 5. The high sorption density of As(V) in coprecipitation with a one hour reaction time suggested that coprecipitation occurs via both adsorption and precipitation. Furthermore, the relationship between residual As(V) and sorption density revealed a BET-type isotherm, with a transition point occurring from a low residual As(V) concentration to a high residual As(V) concentration for initial molar ratios of 0.56 for As/Fe and 1.5 for As/Al. XRD and zeta potential measurements revealed that the transition point from surface complexation to precipitation occurred when the initial As/Fe ratio was 0.3-0.5 and the initial As/Al ratio was 1.5-2. Surface precipitation was clearly identified from XRD and XAFS analysis when the initial As/Fe molar ratio was ≥ 0.4 or As/Al molar ratio was ≥ 1.5 .

Keywords: Arsenate, Ferrihydrite, Aluminum hydroxide, Coprecipitation, Surface complexation

1. Introduction

Arsenic is toxic to animals, including humans, and long-term exposure to arsenic via drinking-water causes cancer of the skin, lungs, urinary bladder, and kidneys, as well as other effects on the skin such as changes in pigmentation and thickening (Ghosha et al., 2008). Acid mine drainage (AMD) containing arsenic is a global environmental problem (Dold, 2008) that also affects Japan, which has many abandoned or closed mines that have been generating AMD for the last few decades (Koide et al., 2012). Several such facilities in Japan produce AMD containing dilute concentrations of arsenic that exceed

Japanese effluent standards (0.1 mg/dm^3) (METI, 2006).

The conventional method for treating AMD is to add a source of alkalinity to increase the pH, resulting in the precipitation of heavy metal pollutants (Kalin et al., 2006). Arsenate (As(V)) or arsenite (As(III)), which are the predominant inorganic arsenic species found in natural aquatic systems (Sadiq, 1997), also coprecipitate with aluminum hydroxide or the hydroxides of heavy metals such as ferrihydrite (Tokoro et al., 2005). Once a mine begins to generate AMD, it generally must be treated indefinitely. However, the disposal of sludge following AMD treatment is also becoming an environmental problem due to the

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potential for toxic substances in the sludge to be re-dissolved. As a result, it is difficult to develop sustainable methods for the treatment of AMD.

This study was conducted to investigate the mechanisms by which dilute As(V) coprecipitates with ferrihydrite or aluminum hydroxide in aqueous solutions. Coprecipitation occurs as a result of a combination of different mechanisms including adsorption, precipitation, storage and solid solution. In the present study, the coprecipitation mechanisms were divided into two categories: surface complexation and surface precipitation. Surface complexation was considered to be the two-dimensional adsorption of As(V) onto the surface of the hydroxide, whereas surface precipitation was used to describe the three-dimensional uptake of As(V) into the ferrihydrite or aluminum hydroxide. Surface precipitation involves ternary adsorption, storage or solid solution that occurs beyond the thermodynamic bulk precipitation range.

The objective of this study was to identify the transition point of As(V) adsorption and surface precipitation in aqueous systems in which the initial As/Fe or As/Al molar ratios were varied from 0.13 to 11 at pH 5. To accomplish this, we conducted batch experiments of coprecipitation or adsorption with ferrihydrite or aluminum hydroxide. The reaction time was fixed at one hour, which is the time commonly used to treat wastewater that contains AMD. We then compared the results and found that an isotherm formed during coprecipitation when the initial As(V) concentration was fixed at 0.15, 0.30 or 0.45 mmol/dm³. A concentration of As(V) of 0.15 mmol/dm³ corresponds to 10 mg/dm³ arsenic, similar to the total arsenic concentration in the AMD from the abandoned Horobetsu sulfur mine. We also measured the zeta potential of As(V) coprecipitated ferrihydrite or aluminum hydroxide formed at fixed initial Fe(III) or Al(III) concentrations with variable initial As(V) concentration. The coprecipitates formed under these conditions were evaluated by X-ray diffraction (XRD) or X-ray absorption fine structure (XAFS).

2. MATERIALS AND METHODS

2.1 Standards and reagents

All chemicals and solutions used in this study were of analytical grade and were purchased from Kanto Chemicals, Inc., Japan. The As(V), Fe(III) and Al(III) solutions were prepared from Na₂HAsO₄·7H₂O, Fe(NO₃)₃·9H₂O and Al(NO₃)₃·9H₂O, respectively. For all experiments, the pH and ionic strength were adjusted by the addition of 0.05 M HNO₃, KOH and KNO₃. Specifically, the pH was fixed at 5 the ionic strength was fixed at 0.05. All experiments were

conducted at 25 °C.

2.2 Coprecipitation experiments

The coprecipitation experiments involved the formation of ferrihydrite or aluminum hydroxide in the presence of As(V). To accomplish this, the Fe(NO₃)₃·9H₂O or Al(NO₃)₃·9H₂O and As(V) solutions were initially combined in 0.5 dm³ of deionized (DI) water to adjust the initial As(V)/Fe(III) or As(V)/Al(III) molar ratio to the target level, after which the pH and ionic strength were adjusted to the target levels. The suspension was then agitated using a magnetic stirrer under pH control for one hour. The suspension was then centrifuged for 20 minutes at 5000 rpm and filtered through a 3 kDa membrane filter. Next, the As(V) concentration in the supernatant was analyzed by ICP-AES using a SPS-4000 atomic emission spectrometer (Seiko Instruments, Japan) with a Hydride Generator Accessory (HYD-10, Seiko Instruments, Japan).

2.3 Adsorption experiments

In this study, simple adsorption experiments using prepared ferrihydrite or aluminum hydroxide were conducted, and the results were then compared with those of the coprecipitation experiments. The adsorption experiments involved the formation of ferrihydrite or aluminum hydroxide and the subsequent adsorption of As(V). To accomplish this, separate Fe(NO₃)₃·9H₂O or Al(NO₃)₃·9H₂O and As(V) solutions at twice the target concentration of Fe(III) or Al(III) and As(V) were initially prepared in 0.5 dm³ of DI water. The pH and ionic strength were then adjusted to the target levels by the addition of HNO₃ and KOH. Next, equal amounts of the Fe(III) or Al(III) solution and As(V) solution were combined and agitated using a magnetic stirrer under pH control for one hour, centrifuged and analyzed for As(V) as described above.

2.4 Zeta potential measurement

To exclude the effects of CO₂, all samples for zeta potential measurements were prepared using N₂ purged DI water in a glove box that was purged with N₂ gas. Suspensions of the products of the coprecipitation experiments, prior to solid/liquid separation, were dispersed in an ultrasonic bath for 5 minutes and then rapidly analyzed. Measurement of the zeta potential was conducted using an electrophoresis light scattering spectrophotometer (ELS-8000, Otsuka Electronics, Japan).

2.5 XRD analysis

The filter residues from the coprecipitation experiments were freeze-dried at -45 °C for 24 h prior to XRD analysis. For comparison with the ferrihydrite and aluminum

hydroxide coprecipitated with As(V), poorly crystalline ferric arsenate and aluminum arsenate were synthesized as reference materials using the procedure described by Jia et al. (2006), with slight modifications. Briefly, a mixture of 0.02 M As(V) and 0.02 M Fe(III) or Al(III) was adjusted from an initial pH of 1.3 to pH 1.8 using KOH solution and then maintained at that pH for one hour. Next, the solid product was separated by filtration, washed with HNO₃-acidified water (pH 2), and freeze-dried at -45 °C.

2.6 XAFS analysis

The X-ray absorption near-edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) measurement were performed at the beam line BL-12C in the Photon Factory (PF) of the National Laboratory for High-Energy Physics, Tsukuba, Japan.

K edge of As was scanned in the range of 11360 to 12965 eV to obtain XANES. The ionization chamber was filled with the Ar (100%) gas to monitor the incident beam, whereas N₂ (100%) gas was used for the transmission beam. Additionally, scanning at K edge of Fe was performed in the range of 6606 to 8209eV for EXAFS analysis. The N₂ (50%) + Ar (50%) gas and N₂ (100%) gas were used for the incident beam and the transmission beam respectively. The higher-order harmonics was reduced by 30% from the maximum incident intensity.

The filter residue obtained from coprecipitation or adsorption experiments was freeze-dried at -45 °C for 12 h, then blended with BN powder and pressed under 20 kN to create the XAFS sample of tablet form.

3. RESULTS AND DISCUSSION

3.1 Comparison of coprecipitation and adsorption characteristics

Figures 1 and 2 show a comparison of the removal ratios of As(V) in the coprecipitation and adsorption experiments conducted at pH 5 using ferrihydrite or aluminum hydroxide. In these experiments, the initial concentration of As(V) was 0.15 mmol/dm³ (10 mg/dm³ arsenic). The data label in these figures is the initial As/Fe molar ratio. In coprecipitation experiments, the As(V) in a solution could be reduced to less than the concentration required by the Japanese effluent standard (0.1 mg/dm³) by the addition of 0.45 mmol/dm³ (30 mg/dm³) Fe(III) or 1.07 mmol/dm³ (29 mg/dm³) Al(III) at pH 5.

For both ferrihydrite and aluminum hydroxide cases, more As(V) was removed during the coprecipitation experiment than the adsorption experiment. This indicates that the As(V) coprecipitation mechanism involves more

than simple adsorption.

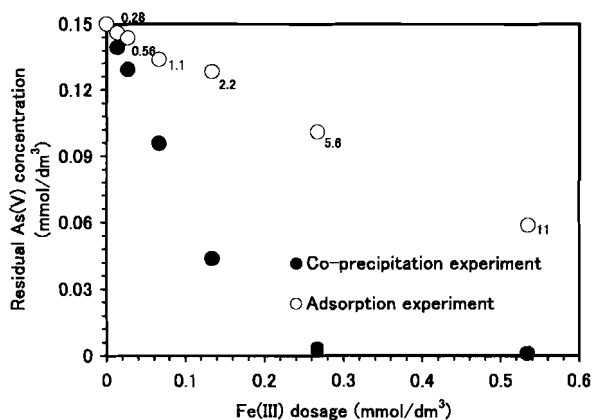


Fig.1 Comparison of the coprecipitation and adsorption experimental results using ferrihydrite at pH 5.

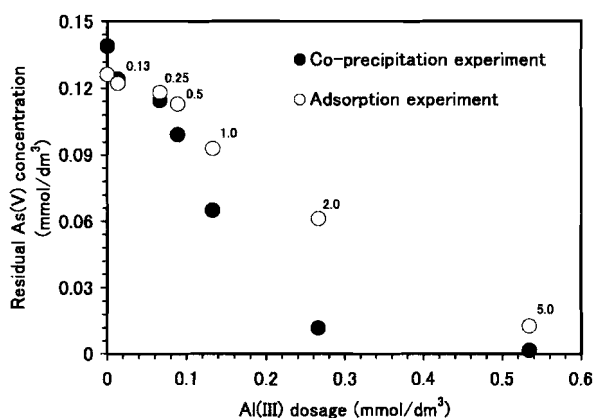


Fig.2 Comparison of the coprecipitation and adsorption experimental results using aluminum hydroxide at pH 5.

3.2 Relation between sorption density and residual As(V) concentration

Figures 3 and 4 show the sorption density for the As(V) coprecipitation or adsorption experiments with ferrihydrite or aluminum hydroxide obtained at pH 5. In these experiments, the initial concentration of As(V) was fixed at 0.15, 0.30 or 0.45 mmol/dm³, while the Fe(III) or Al(III) concentrations were changed to give the desired initial target As/Fe or As/Al molar ratio.

As(V) coprecipitation with ferrihydrite or aluminum hydroxide with a one hour reaction time produced a BET-type isotherm for all initial concentrations of As(V) evaluated in this study. On the other hand, As(V) adsorption to ferrihydrite or aluminum hydroxide produced a Langmuir-type isotherm. It has often been proposed that As(V) adsorption to ferrihydrite or goethite produces a Langmuir or Freundlich-type isotherm (Hsia, 1994). The BET-type isotherm of As(V) observed in this study indicates that the mechanism by which coprecipitation of As(V) with

ferrihydrate or aluminum hydroxide occurs when there is a one hour reaction time involves more than simple adsorption onto the surface of the hydroxide. Specifically, these findings indicate that some three-dimensional uptake, such as precipitation or the formation of several layers of adsorbate, occurs.

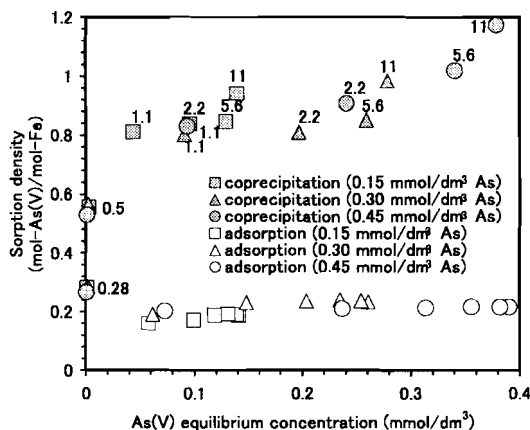


Fig.3 Relation between the sorption density and the residual As(V) concentration at pH 5 during As(V) coprecipitation or adsorption with ferrihydrate.

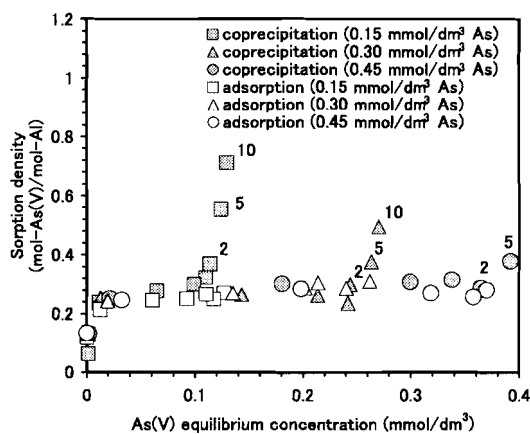


Fig.4 Relation between the sorption density and the residual As(V) concentration at pH 5 during As(V) coprecipitation or adsorption with aluminum hydroxide.

In the ferrihydrate case, higher sorption densities were observed in coprecipitation experiments compared to adsorption experiments. On the other hand, in the case of aluminum hydroxide, similar sorption densities were observed for coprecipitation and adsorption experiments when the initial As/Fe molar ratio was less than 1.5. This indicates that the mechanism of coprecipitation of As(V) with ferrihydrate involves a greater amount of three-dimensional uptake beyond simple adsorption than for coprecipitation of As(V) with aluminum hydroxide. The large sorption density observed for As(V) coprecipitation with ferrihydrate indicates that ferrihydrate is a better agent

than aluminum hydroxide for coprecipitation treatment of wastewater containing As(V).

3.3 Results of zeta potential measurement

Figures 5 and 6 show the zeta potential of As(V) coprecipitated ferrihydrate or aluminum hydroxide as a function of the sorption density of As(V) to ferrihydrate or aluminum hydroxide at pH 5. The relationship between the zeta potential of As(V) adsorbed ferrihydrate or aluminum hydroxide and the sorption density is also shown in these figures for comparison.

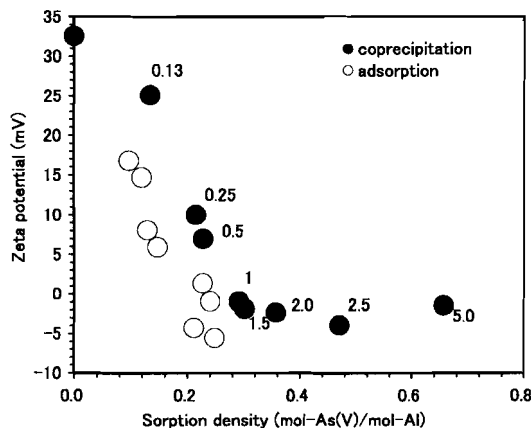


Fig.5 Zeta potential and the As(V) sorption density during As(V) coprecipitation or adsorption with ferrihydrate.

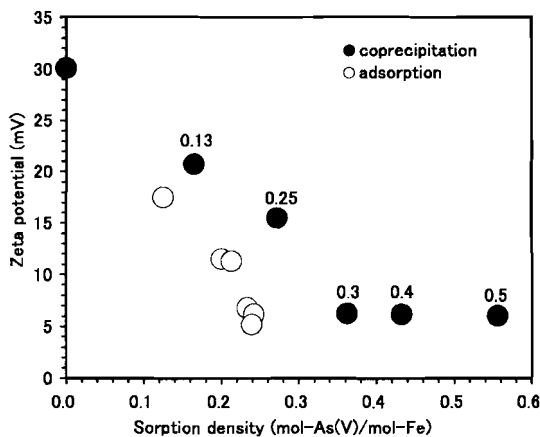


Fig.6 Zeta potential and the As(V) sorption density during As(V) coprecipitation or adsorption with aluminum hydroxide.

These figures show that a linear relationship between the zeta potential and the As(V) sorption density without any breaking point is observed for As(V) adsorption with ferrihydrate or aluminum hydroxide. However, the curves describing the relationship between zeta potential and As(V) sorption for As(V) coprecipitation decreased rapidly at low values of the sorption density and changed much less rapidly

at higher sorption densities. This break in the slope of the curves between zeta potential and sorption density occurred when the initial molar ratio of As/Fe was 0.3 or As/Al was 1.5. These findings suggest that the dominant mechanism at the surface when As(V) is coprecipitated was simple adsorption at low initial As/Fe or As/Al molar ratios and surface precipitation at high initial As/Fe or As/Al molar ratios.

3.4 Results of XRD analysis

Figures 7 show a comparison of the XRD patterns for the coprecipitate formed from As(V) with ferrihydrite as a function of the initial molar ratio of As/Fe at pH 5.

As shown in Figure 7, when the coprecipitated products were generated using an initial As/Fe ratio of 0.13 or 0.25, the XRD patterns were very similar to those of ferrihydrite, although the two peaks corresponding to ferrihydrite became broader and weaker. This could have occurred because the presence of increasing amounts of As(V) promoted the formation of ferrihydrite with lower crystallinity and smaller particle size. At these concentrations, the mechanism of coprecipitation of As(V) is predominantly adsorption to the surface of ferrihydrite. We also evaluated the XRD patterns of As(V) adsorbed ferrihydrite at different pH values and initial As/Fe molar ratios and found that they were also similar to the pattern for ferrihydrite, with the two peaks corresponding to ferrihydrite becoming broader and weaker as the initial As/Fe molar ratio increased. In contrast, when the initial As/Fe ratio was 0.5, the first peak of ferrihydrite became broader and shifted toward that of poorly crystalline ferric arsenate, and furthermore, the XRD peaks formed when the initial As/Fe ratio was >0.5 were located at the same positions as those of poorly crystalline ferric arsenate. In these cases, the mechanism of coprecipitation of As(V) is predominantly precipitation of ferric arsenate, which would involve ternary adsorption, storage or solid solution occurring beyond the thermodynamic bulk precipitation range.

Although the figure is not shown here due to limitations of space, we got same trend in the case of aluminum hydroxide. That is, XRD patterns of the coprecipitated products were similar to aluminum hydroxide in 0.25-1.0 of initial As/Al, whereas those were similar to poorly crystalline aluminum arsenate in 2.0 or 5.0 of initial As/Al.

The initial molar ratios at which these transitions in zeta potential slope occurred correspond to the initial molar ratios of As/Fe or As/Al where transitions in the XRD patterns also occurred, implying that the mechanism of interaction changes at a molar ratio of 0.3 for As(V) and ferrihydrite and a molar ratio of 1.5 for As(V) and aluminum hydroxide.

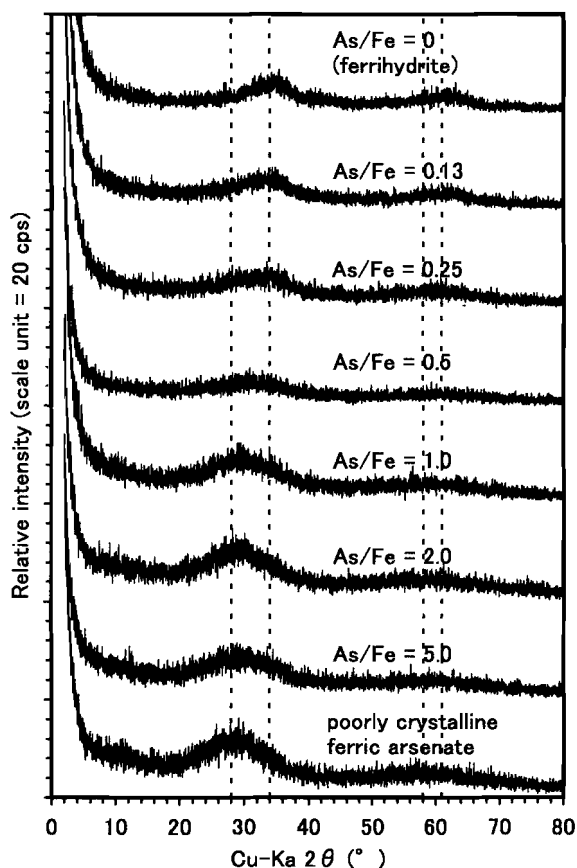


Fig.7 Comparison of the XRD patterns of As(V) coprecipitated ferrihydrite formed at pH 5 with those of the reference materials (ferrihydrite and poorly crystalline ferric arsenate).

3.5 Results of XAFS analysis

Figure 8 shows As-K-edge XANES spectra of As(V) coprecipitates with ferrihydrite, As(V) adsorbed ferrihydrite and poorly crystalline ferric arsenate. All spectrums give two first peaks at 11868 and 11881 Å. As shown in Figure 8, XANES spectra of As(V) coprecipitates with ferrihydrite gradually changed from that of As(V) adsorbed ferrihydrite to that of ferric arsenate as the initial Fe/As molar decreased. These findings indicated the coprecipitates are a mixture of amorphous ferric arsenate and As(V) adsorbed ferrihydrite. To know the weight ratio of surface precipitation and surface complexation in As(V) coprecipitates, XAFS spectra of As(V) coprecipitates with ferrihydrite was fitted using that of amorphous ferric arsenate and As(V) adsorbed ferrihydrite between 11870 and 11910 Å. As shown in Table 1, it is found that ratio of amorphous ferric arsenate becomes larger as the initial Fe/As molar ratio decreases and estimated weight ratio of amorphous ferric arsenate in As(V) coprecipitates became above 0.5 when the initial molar ratio of $As/Fe \geq 0.5$ was used. These results corresponded with the results of zeta potential and XRD measurements.

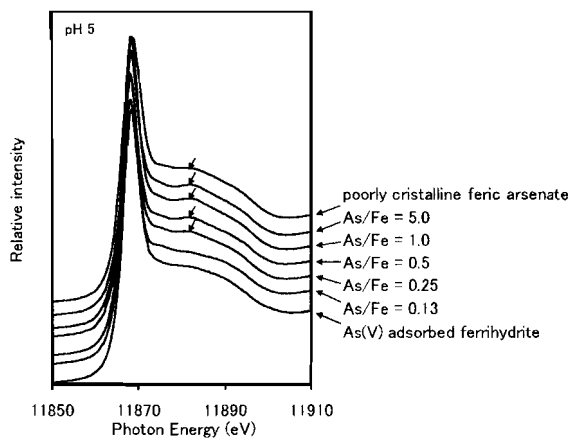


Fig.8 Normalized As K-edge XANES spectra of As(V) adsorbed ferrihydrite, poorly crystalline ferric arsenate and As(V) co-precipitated ferrihydrite obtained at pH 5.

Table 1 Pattern fitting results for XANES and EXAFS spectra of As(V) co-precipitated ferrihydrite: reference materials are As(V) adsorbed ferrihydrite and poorly crystalline ferric arsenate.

As/Fe	XANES		EXAFS	
	ad	fa	ad	Fa
0.13	0.69	0.31	0.79	0.21
0.25	0.51	0.49	0.61	0.39
0.5	0.44	0.56	0.49	0.51
1	0.37	0.63	0.30	0.70
2	0.19	0.81	0.20	0.80

ad, As(V) adsorbed ferrihydrite; fa, ferric arsenate

EXAFS curve fitting results showed that there are three kinds of surface complexes for As-Fe bonds; i.e. bidentate-mononuclear surface complex (distance between As and Fe is 2.85 Å), bidentate-binuclear surface complex (3.24 Å) and monodentate surface complex (3.59 Å). The coordination number for 2.85 Å of As-Fe bond increased and it for 3.24 Å of As-Fe bond decreased with decreasing the initial Fe/As molar ratio while it for 3.59 Å of As-Fe bond was very small value and unaffected by the initial As/Fe molar ratio. These findings show that bidentate-mononuclear surface complex of As(V) to ferrihydrite was gradually increased and bidentate-binuclear surface complex of As(V) to ferrihydrite was gradually decreased as the initial Fe/As molar ratio decreased.

4. CONCLUSION

In this study, we investigated the mechanism of dilute As(V) coprecipitation by ferrihydrite or aluminum hydroxide using a one hour reaction time for a wide range of initial As/Fe or As/Al molar ratios.

For both As(V) coprecipitation with ferrihydrite or aluminum hydroxide, a BET-type sorption isotherm was

obtained whereas a Langmuir-type sorption isotherm was obtained in As(V) adsorption experiments. These results suggested that As(V) sorption mechanism in coprecipitation experiments is not only simple As(V) adsorption. XRD and XAFS analyses and zeta potential measurements showed that As(V) complexation to the surface of ferrihydrite was dominant when an initial molar ratio of $As/Fe \leq 0.25$ was used, whereas precipitation of amorphous ferric arsenate was formed when an initial molar ratio of $As/Fe \geq 0.5$ was used. On the other hand, in the case of As(V) coprecipitation with aluminum hydroxide, As(V) complexation to the surface of aluminum hydroxide was dominant when an initial molar ratio of $As/Al \leq 1.0$ was used, whereas precipitation of amorphous aluminum arsenate occurred when the initial molar ratio of $As/Al \geq 1.5$.

5. REFERENCES

- Ghosh, P., Banerjeca, M., Giri, A. K. and Raya, K. (2008). Toxicogenomics of arsenic: Classical ideas and recent advances. *Mutat., Res.*, 659, 293-301pp.
- Dold, B. (2008). Sustainability in metal mining: from exploration, over processing to mine waste management. *Rev. Environ. Sci. Biotechnol.*, 7, 275-285pp.
- Koide, R., Tokoro, C., Murakami, S., Adachi, T. and Takahashi, A. A Model for Prediction of Neutralizer Usage and Sludge Generation in the Treatment of Acid Mine Drainage from Abandoned Mines: Case Studies in Japan. *Mine Water Environ.*, in press.
- Japanese Ministry of Economy, Trade and Industry (METI), (2006). "Kougai Boushi no Gijutsu to Houki, Suishitu (in Japanese)", Maruzen: Tokyo, 593-926pp.
- Kalin, M., Fyson, A. and Wheeler, W. N. (2006). The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. *Sci. Total. Env.* 366, 395-408pp.
- Sadiq, M. (1997). Arsenic chemistry in soils. *Water Air Soil Pollut.* 1997, 93, 117-136.
- Tokoro, C., Shimizu, T., Hirai, K., Badulis, G. C. and Sasaki, H. (2005). Application of Surface Complexation Model for Dilute As Removal in Wastewater by Fe(III) or Al(III) Salts. *J. MMIJ*, 121, 399-406pp.
- Jia, Y., Xu, L., Fang, Z. and Demopoulos, G. P. (2006). Observation of surface precipitation of arsenate on ferrihydrite, *Environ. Sci. Technol.* 40, 3248-3253pp.
- Hsia, T. H., Loa, S. L., Lid, C. F. and Lee, D. Y. (1994). Characterization of arsenate adsorption on hydrous iron oxide using chemical and physical methods, *Colloids Surf.*, A. 85, 1-7pp.