

Report for 2003TX91B: Adsorption, Desorption, and Stabilization Behavior of Arsenic on Al³⁺-substituted Fe³⁺-Hydrous Oxides

- Conference Proceedings:
 - Masue, Y., R.H. Loeppert, G.N. White, and T. Kramer. 2003. Adsorption, desorption, and stabilization behavior of arsenic(V) on Al³⁺ substituted Fe³⁺ oxides. P.88-89. In Abstracts, the 7th International Conference on the Biochemistry of Trace Elements, Uppsala, Sweden, 15-18 June.2003
- Other Publications:
 - Masue, Y., R.H. Loeppert, and T. Kramer. 2003. Influence of counterion on adsorption and desorption behavior of arsenic on ferrihydrite and Al-substituted analogs was presented at American Society of Agronomy annual meeting in Denver, CO, 2-6 November. 2003

Report Follows

Adsorption, Desorption, and Stabilization Behavior of
Arsenic on Ferrihydrite and Al-substituted Analogs.

Progress Report

February 24, 2004

Yoko Masue¹, Richard Loeppert¹, and Timothy Kramer²

Department of Soil and Crop Sciences¹
Department of Civil Engineering²

Texas A&M University
College Station, TX 77843

1. Research Progress

Introduction

Arsenic introduced by natural processes or human activities can result in the contamination of water and soils. The removal of arsenic from water is necessary if the water is to be consumed by humans (Nriagu, 2002). Counterion effect has been recognized as a possible factor influencing ligand adsorption reactions in aqueous systems. Understanding the counterion effect could help to comprehend mobility of arsenic in a variety of environments to improve treatment of arsenic-containing wastewater, and to stabilize residual materials. Furthermore, Al or Fe hydroxides are commonly used as adsorption agents in water treatment systems (Hering et al., 1996). However, there has been very little attention to mixed Fe/Al oxides as adsorbents. The use of mixed Fe/Al systems could present an interesting alternative for As treatment and disposal, since Al hydroxide is not affected by redox processes. In addition, most Fe oxides present in soils are Al substituted (Schwertmann and Taylor, 1989); therefore, it is essential to understand the adsorption behavior of Al substituted Fe oxides to fully understand As retention in soils.

Objectives

To investigate the possible use of mixed Fe/Al adsorbents in water treatment by studying:

- Adsorption and desorption of As
- The effect of counterions, Ca^{2+} versus Na^+ , and counterion concentration on As retention
- Mineralogy of precipitated Fe/Al hydroxide phases and their incubation products

Materials and Methods

I. Synthesis of ferrihydrite and Al-substituted analogs

Al-substituted ferrihydrite samples were prepared at 1:0, 97:3, 9:1, 8:2, 7:3, 6:4, 5:5, and 0:1 Fe:Al molar ratios by varying the $\text{Fe}(\text{NO}_3)_3:\text{Al}(\text{NO}_3)_3$ molar ratio in the method for synthesis of two-line ferrihydrite (Schwertmann and Cornell, 1991). An x-ray diffraction pattern of each product was obtained to identify its mineralogical composition. Al substituted hydrous oxides were also prepared at 1:0, and 8:2 Fe:Al molar ratios by using saturated $\text{Ca}(\text{OH})_2$ or 0.1 M NaOH to adjust pH to 7-8, to obtain systems with Ca or Na exclusively. The volumes of saturated $\text{Ca}(\text{OH})_2$ or 0.1 M NaOH solution needed were recorded to determine the accurate concentrations of Ca and Na in the systems. The

saturated $\text{Ca}(\text{OH})_2$ solution used was prepared under N_2 atmosphere at room temperature, and it was titrated with HCl to determine its concentration

II. Adsorption envelopes of As^{V} on Al-substituted ferrihydrite samples at different Fe: Al molar ratios

Adsorption envelopes of As^{V} on the Fe/Al oxide products were obtained in 0.1 M NaCl at a $\text{As}:(\text{Fe}+\text{Al})$ molar ratio of 0.05:1. The pH values of separate samples were adjusted between 3 and 11 by adding HCl or NaOH , and suspensions were equilibrated 24 h on a platform shaker. Upon completion of the reaction, samples were centrifuged, and the pH of the supernate was obtained. The samples were filtered through 0.2 mm nominal pore size membrane filters.

III. Adsorption envelopes of As^{V} and As^{III} in Ca and Na systems

Adsorption envelopes of As^{V} on the Fe/Al oxide products in Ca and Na systems were obtained. Ca and Na concentrations were adjusted using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and NaNO_3 salt solutions. The pH values of separate samples were adjusted between 3 and 11 by adding HNO_3 or NaOH and equilibrated 24 h on a rotary shaker. Upon the completion of the reaction, samples were centrifuged, and the pH of the supernate was obtained. The samples were filtered through 0.2 mm nominal pore size membrane filters.

IV. Adsorption isotherms of As^{V} in Ca and Na systems

Adsorption isotherms of As^{V} on the Fe/Al oxide products in Ca and Na systems were obtained at pH 5 and pH 8 in 0.1 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and NaNO_3 with $\text{As}:(\text{Fe}+\text{Al})$ molar ratios ranging from 0.0125:1 to 0.5:1. The pH values of separate samples were adjusted by adding HNO_3 or NaOH , and the volume of each sample was brought to 30 ml. Samples were equilibrated 24 h on a rotary shaker. Upon completion of the reaction, samples were centrifuged and filtered through 0.2 mm nominal pore size membrane filters.

V. Stability of ferrihydrite and Al-substituted analogs

Stabilities of 1:0 and 8:2 Fe:Al oxides were examined at pH 4 and 10. A set of samples was prepared to give an $\text{As}:(\text{Fe}+\text{Al})$ molar ratio of 0.05:1, and the pH was adjusted by adding HCl or NaOH . A set of samples without $\text{As}(\text{V})$ was also prepared with identical oxide concentrations. Samples were incubated at 70°C , and subsamples were taken after 12, 24, 48, and 96 h. $\text{As}(\text{V})$ was added to the subsamples which were incubated without $\text{As}(\text{V})$, and deionized water was added to the samples which were incubated with $\text{As}(\text{V})$ to ensure equal concentrations of As, Fe and Al. The subsamples were adjusted to pH 7.0 with HCl or NaOH , and they were aged at room temperature for 2 h to allow adsorption of As. Samples were centrifuged, filtered, and analyzed for total dissolved As by FI-HG-AAS. Residual oxides were washed with deionized water, and analyzed using XRD. Samples were also extracted with ammonium oxalate at pH 3 in the dark to determine the proportion of poorly crystalline Fe oxide.

VI. Arsenic analysis

As was analyzed using FI-HG-AAS. 5 M HCl and 15 % NaBH_4 + 5 % NaOH were used as eluents during flow injection to convert As species present in solution to arsine. As^{V}

standard solution was used for total As analysis with the As^V experiments and As^{III} standard solution was used for total As analysis with the As^{III} experiments. The matrices of the standard were deionized water.

Results and Discussions

I. Synthesis of ferrihydrite and Al-substituted analogs

Al was incorporated into the poorly crystalline ferrihydrite structure up to approximately 0.30 Al:(Fe+Al) molar ratio (Figure 1); however, a trace of gibbsite, crystalline Al hydroxide, was observed at 0.30 Al:(Fe+Al). Gibbsite was observed as a coprecipitated product with Al:(Fe+Al) molar ratios greater than 0.40 (Figure 1). The 8:2 oxide resulted in a XRD pattern almost identical to that of ferrihydrite. This poorly crystalline phase is desirable in water treatment as it provides high surface area.

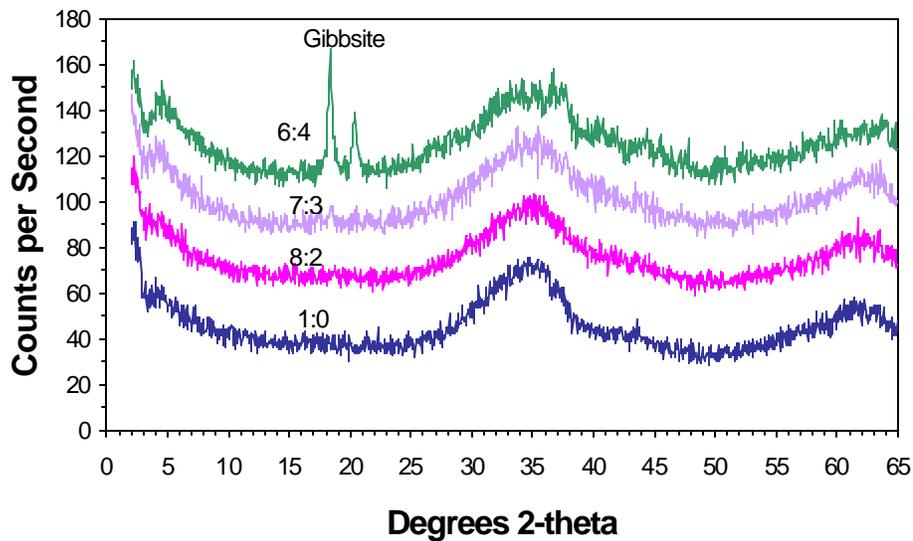


Figure 1. XRD patterns of ferrihydrite and Al-substituted analogs.

II. Adsorption envelopes of As^V on Al-substituted ferrihydrite samples at different Fe: Al molar ratios

Strong retention of As^V was observed throughout the pH range of 3 to 6.5 with ferrihydrite and its Al-substituted analogs (Figure 2). Adsorption of As^V on Al hydroxide (0:1) was much less compared to that on the Fe/Al oxides (Figure 2). This study indicates that Al substitution did not result in a decrease in arsenic retention.

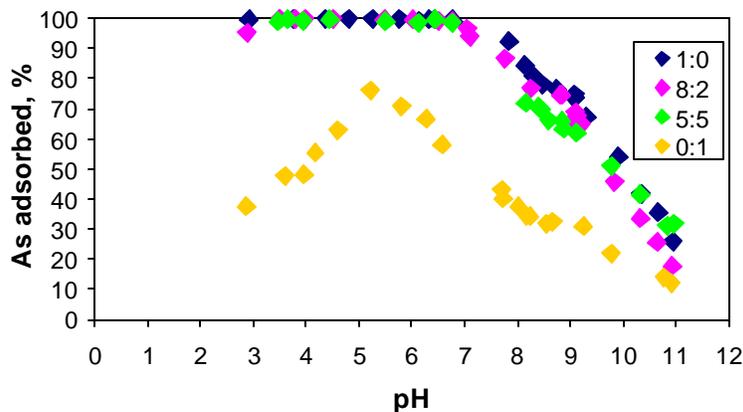


Figure 2. Adsorption envelopes of As^{V} on Al-substituted ferrihydrite at different Fe:Al molar ratios.

III. Adsorption envelopes of As^{V} and As^{III} in Ca and Na systems

As^{V} retention was greater in the Ca system compared to that in the Na system (Figures 3 and 4). Strong retention of As^{V} was observed throughout the pH range of 3 to 6 with 0.1:1 As:(Fe+Al) molar ratio, and 3 to 8 with 0.025:1 As:(Fe+Al) molar ratio (Figures 3 and 4). Significant effect of Al substitution and counterion concentration were not observed (Figures 3, 4, 5, and 6). This result suggests that the Ca in water treatment might be beneficial to improve the retention of arsenic on residual material; although, Na is most commonly used in current conventional water treatment plants.

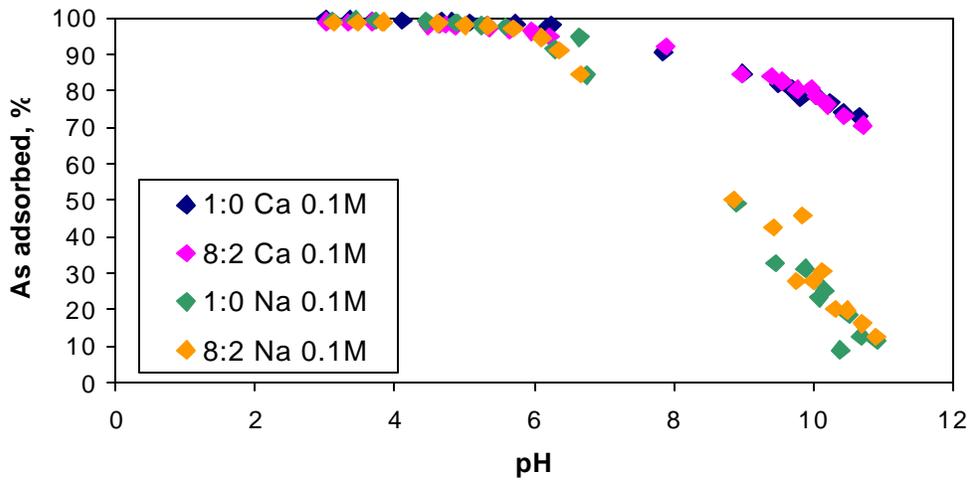


Figure 3. Adsorption envelopes of As^{V} in 0.1 M Ca and Na at a 0.1:1 As:(Fe+Al) molar ratio.

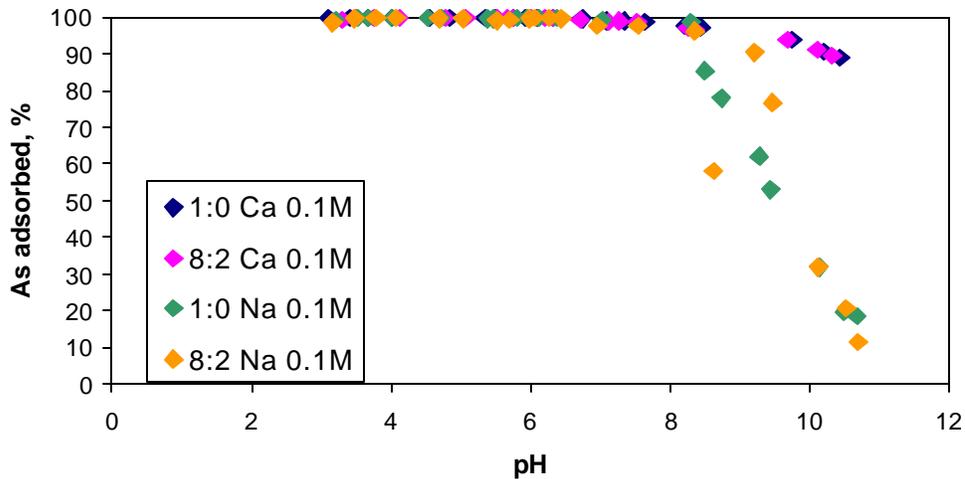


Figure 4. Adsorption envelopes of As^{V} in 0.1 M Ca and Na at a 0.025:1 As:(Fe+Al) molar ratio.

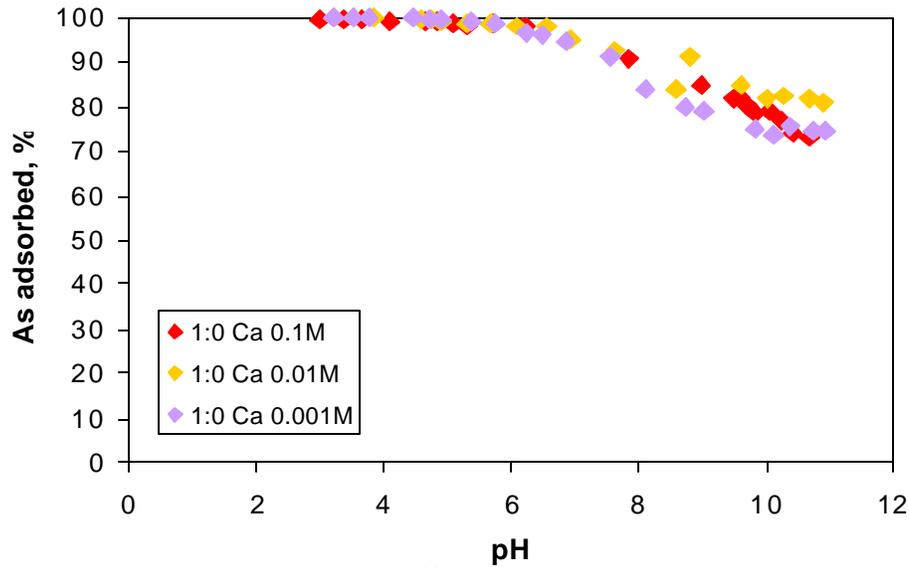


Figure 5. Adsorption envelopes of As^{V} in 0.1, 0.01, and 0.001M Ca at a 0.1:1 As:Fe molar ratio.

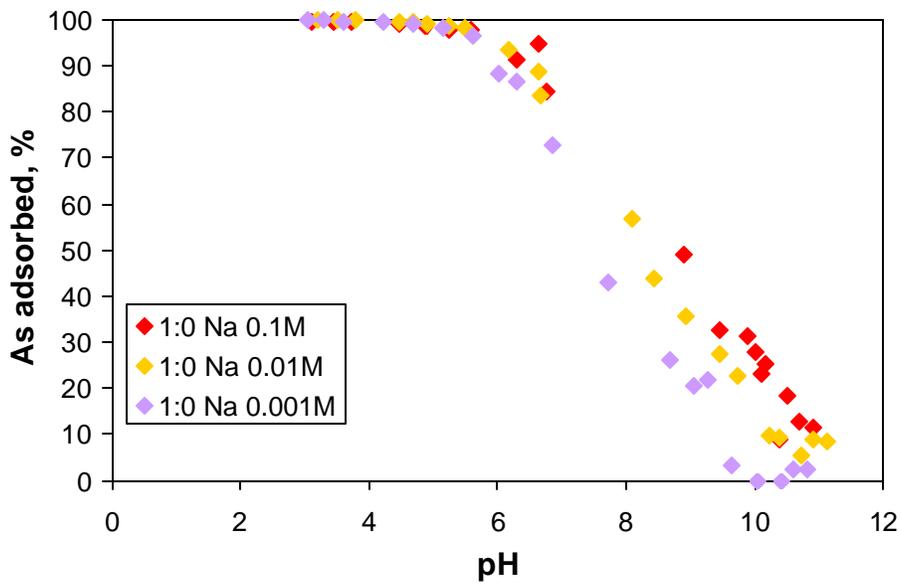


Figure 6. Adsorption envelopes of As^{V} in 0.1, 0.01, and 0.001M Na at 0.1:1 As:Fe molar ratio.

IV. Adsorption isotherms of As^V in Ca and Na systems

Ca systems had higher adsorption capacity compared to Na systems at both pH 5 and 8 (Figures 7, and 8). At pH 5, the effect of Al substitution was negligible (Figure 7). At pH 8, pure Fe oxides had greater retention of As^V at most As:(Fe+Al) molar ratios (Figure 8).

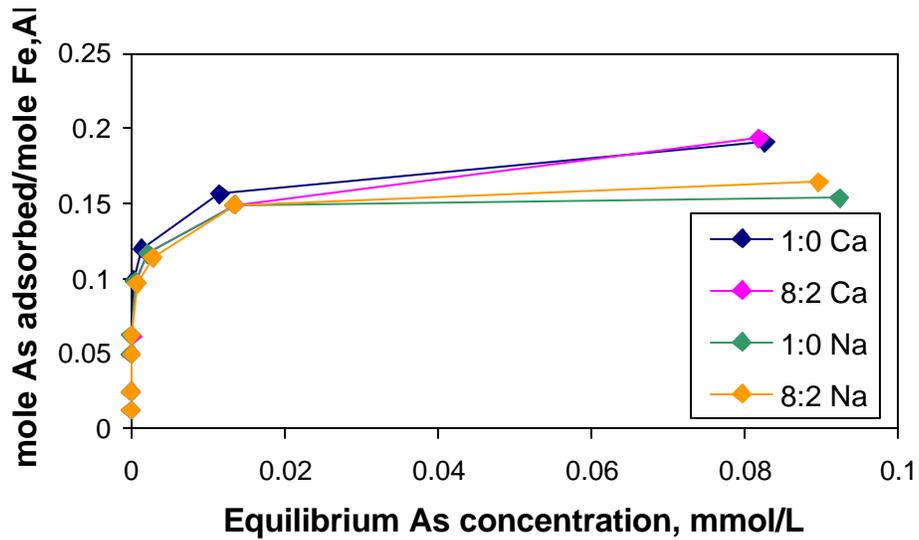


Figure 7. Adsorption isotherms of As^V at pH 5.

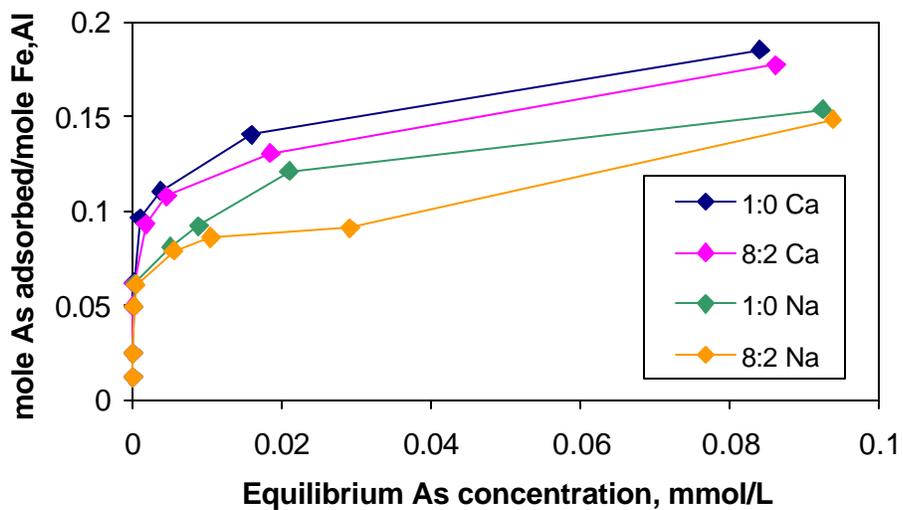


Figure 8. Adsorption isotherms of As^V at pH 8.

V. Stability of ferrihydrite and Al-substituted analogs

Ammonium oxalate extractable Fe is a portion Fe that is poorly crystalline. Poorly crystalline oxide is desirable for water treatment as it provides higher surface area for As adsorption. This study indicates that Al substitution slowed the transformation of ferrihydrite to a crystalline phase (Table 1 and Figure 9, 10 and 11). In addition, arsenic retarded the transformation of ferrihydrite to a crystalline phase (Table 1). Oxides equilibrated at pH 4 transformed more slowly than those equilibrated at pH 10 (Figure 10 and 11).

Treatment	Incubated with As	Incubated without As
	AOE Fe/Total Fe, %	
1:0 pH 10	97	0
1:0 pH 4	95	53
8:2 pH 10	99	64
8:2 pH 4	100	100

Table 1. Proportion of ammonium oxalate extractable Fe over total Fe, %.

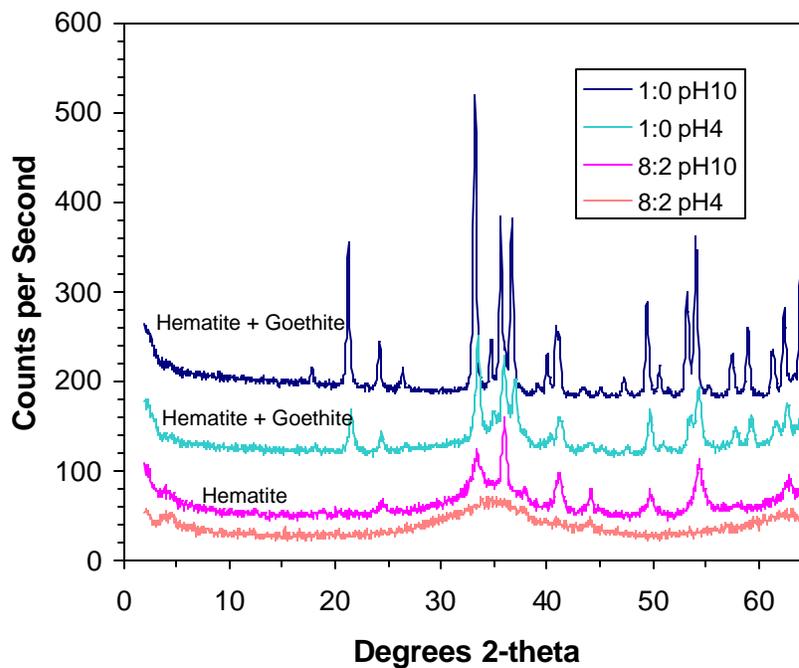


Figure 9. XRD patterns of the oxides, incubated without As for 96h.

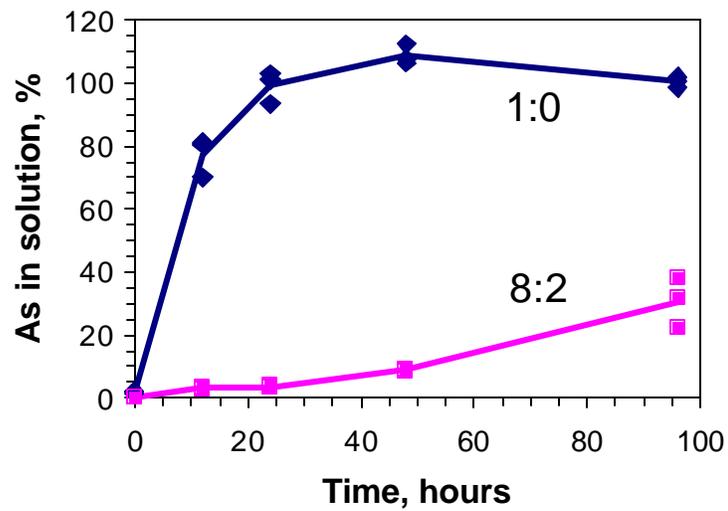


Figure 10. As remaining in solution,%, as a function of time for the oxides originally incubated without As at pH 10.

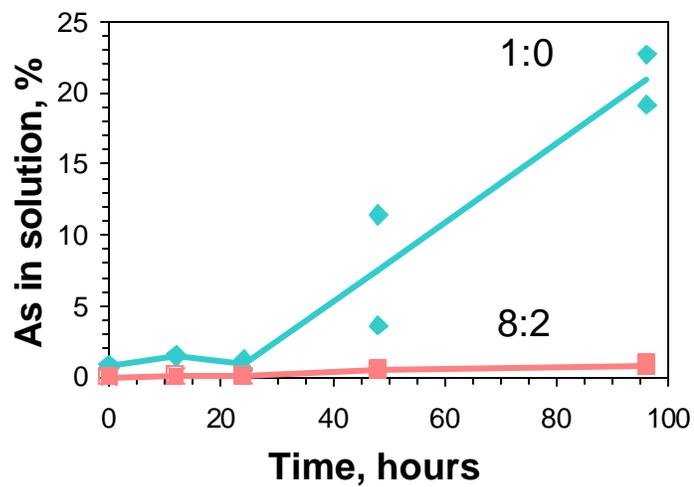


Figure 11. As remaining in solution,%, as a function of time for the oxides originally incubated without As at pH 4

Conclusions

Al was completely incorporated in the poorly crystalline structure up to 20%. Al substitution did not result in a significant decrease in arsenic retention at 0.05:1 As:(Fe+Al) molar ratio. Retention of both As^V and As^{III} were substantially greater in the presence of Ca counterion compared to Na counterion especially above pH 7. Ca counterion in water treatment might be useful to improve the retention of arsenic on residual material.

Coprecipitation of Al³⁺ during precipitation of poorly crystalline Fe/Al hydroxide resulted in a product that was more stable against transformation to well crystalline goethite or hematite. The Fe/Al mixed oxides provided a better retention of As with time compared to pure Fe oxide due to the higher surface area. The Fe/Al mixed oxides could be an effective alternative for water treatment.

Research in Progress

Adsorption behavior of As^{III} are being examined with ferrihydrite and Al-substituted analogs. As^{III} adsorption in Ca and Na systems will be also studied. In addition, desorption behavior of As^V and As^{III} will be examined with phosphate and sulfate.

The use of Si to improve the stability of the residual material with Al-substituted ferrihydrite will be investigated. Si retards the transformation of poorly crystalline Fe oxide to crystalline Fe oxide such as goethite; therefore, the presence of Si might help maintain the surface area to provide site for binding. We will also explore the possibility of synthesizing porous media using Si and Al-substituted ferrihydrite.

References

- Hering, J.G., P.Y. Chen, J.A. Wilkie, M. Elimelech, and S. Liang. 1996. Arsenic removal by ferric chloride. *Jour. AWWA*. 88:155-167.
- Meng X., Korfiatis G.P., Jing C., and Christodoulatos C. (2001) Redox transformations of arsenic and iron in water treatment sludge during aging and TCLP extraction. *Environ. Sci. Technol.* 35, 3476-3481.
- Nriagu, J.O. 2002 Arsenic poisoning through the ages, p. 1-26. *In* W.T. Frankenberger (ed.) *Environmental chemistry of arsenic*. Marcel Dekker, Inc. New York, NY
- Schwertmann, U., and R.M. Cornell. 1991 Iron oxides in the laboratory. VCH, Weinheim.
- Schwertmann, S., and R.M. Tylor. 1989 Iron Oxides, p. 379-438. *In* J.B. Dixon, and S.B. Weed (ed.) *Minerals in Soil Environments*. SSSA Book Series: 1, Soil Sci. Soc. Am., Madison, Wisconsin

2. Publications and presentations

- Masue, Y., R.H. Loeppert, G.N. White, and T. Kramer. 2003. Adsorption, desorption, and stabilization behavior of arsenic(V) on Al³⁺ substituted Fe³⁺ oxides. P.88-89. *In*

Abstracts, the 7th International Conference on the Biochemistry of Trace Elements, Uppsala, Sweden, 15-18 June.2003

Masue, Y., R.H. Loeppert, and T. Kramer. 2003. Influence of counterion on adsorption and desorption behavior of arsenic on ferrihydrite and Al-substituted analogs was presented at American Society of Agronomy annual meeting in Denver, CO, 2-6 November. 2003

3. Budget

Provided funds were entirely expended on the tuition, travel expenses to present the research, and the books.

4. Degree program

Yoko Masue is expected to complete M.S. in Soil Science in August 2004.