

XAFS investigation for As(V) coprecipitation mechanism with ferrihydrite

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Introduction

XAFS analysis were conducted to investigate the As(V) coprecipitation mechanism with ferrihydrite (γ -FeOOH), if treatment of acid mine drainage containing dilute As(V) using coprecipitation is feasible. We already confirmed that the high sorption density of As(V) to ferrihydrite in coprecipitation with 1-hour reaction time at pH 5 or 7 was achieved when the initial As(V) concentration was dilute such as 0.02-0.9 mmol/dm³ and the initial As/Fe ratio was over 0.4. We also conducted XRD analysis and zeta potential measurement which revealed that the mechanism of As(V) coprecipitation to ferrihydrite changed at 0.4 of the initial As/Fe molar ratio; i.e., As(V) was primarily adsorbed as a surface complex when the initial molar ratio was As/Fe<0.4, while a ferric arsenate and surface complex was formed when this ratio was ≥ 0.4 .

The objective of study was to identify the mechanism of As(V) coprecipitation to ferrihydrite more briefly using XAFS analysis on As K edge.

Experimental

Coprecipitation test

We conducted batch experiments of coprecipitation with ferrihydrite. All chemicals and solutions used in this study were of analytical grade and were purchased from Kanto Chemicals, Inc., Japan. The As(V) and Fe(III) solutions were prepared from Na₂HAsO₄·7H₂O and Fe(NO₃)₃·9H₂O, respectively. The pH was fixed at 5 or 7 and the ionic strength was fixed at 0.05 using HNO₃ and KOH. The initial concentration of Fe(III) was fixed at 0.18 mmol/dm³ and the concentration of As(V) was changed to attain the target initial As/Fe molar ratio of 0.13-5. The filter residue was freeze-dried, pelletized and applied to the XAFS analysis.

Preparation of reference materials

Poorly crystalline ferric arsenate and As(V) adsorbent to ferrihydrite was synthesized as a reference material. poorly crystalline ferric arsenate was prepared using the procedure described by Jia et al. (1), with slight modification.

The adsorption experiments involved the formation of ferrihydrite particles and the separate adsorption of As(V).

Results and Discussion

Both of XANES and EXAFS analysis on K-edge of As showed As(V) coprecipitates with ferrihydrite was mixture of As(V) adsorbed ferrihydrite and poorly

crystalline ferric arsenate. Estimated weight ratio of amorphous ferric arsenate in As(V) coprecipitates became above 0.5 when the initial molar ratio of As/Fe ≥ 0.5 was used. These results corresponded with results from XRD analysis and zeta potential measurement. EXAFS analysis assuming one surface complex for As-Fe bond showed the coordination number of As to Fe in As(V) coprecipitates increased with increasing the initial molar ratio of As/Fe.

Moreover, we also conducted EXAFS analysis assuming three kinds of surface complexes for As-Fe bond. Figure shows full shell, k³-weighted back transformed spectra (0 to 4 Å in the FT spectra) of As(V) adsorbed ferrihydrite (ad) and poorly crystalline ferric arsenate (fa). Solid line is the experimental spectra, dashed line is the best fit line for three type of surface complexes and gray dashed line is the best fit line for one type of surface complex. This figure suggested EXAFS analysis assuming three kinds of surface complexes was fit more successfully to experimental results than assuming only one surface complex. Analysis results of As(V) coprecipitates showed the coordination number for 2.85 Å of As-Fe bond increased and it for 3.24 Å of As-Fe bond decreased with increasing the initial As/Fe molar ratio.

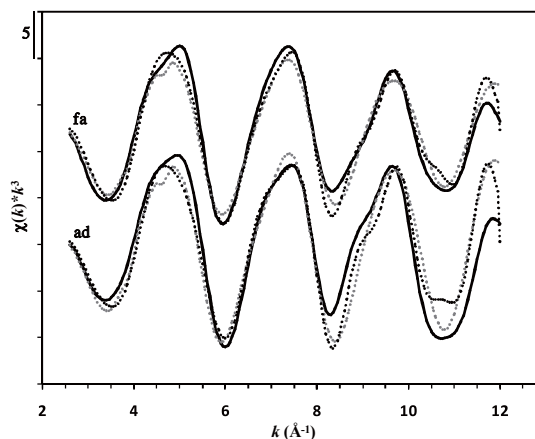


Figure 1: k³-weighted back transformed spectra

References

- [1] Y. Jia et al., Geochim. Cosmochim. Acta. 71, 1643(2007).

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