

An XAFS Study of Zn Sorption Mechanisms on HFO over Extended Reaction Times

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Introduction

To select appropriate management options and cleanup strategies for contaminated soil environments, an understanding of metal speciation and sorption products is important. This study was conducted to understand sorption mechanisms, identify sorption species, and describe the local chemical environment of zinc sorbed on hydrous iron oxide (HFO) surfaces over extended reaction time. Findings from this research will provide a fundamental understanding of metal sorption reactions and mechanisms in soil environmental systems and will ultimately help in making environmentally sound planning, management, assessment, and strategic decisions for cleanup processes.

Methods and Materials

Batch sorption experiments of Zn onto HFO were conducted at room temperature with a fixed pH of 7.0 in 0.1 M NaNO₃. For the system open to atmospheric CO₂, the reactor suspension was mixed by a stirrer and purged by air, and for the CO₂-free system, high-purity N₂ gas was purged and mixed by a stirrer inside a N₂ chamber. Fresh HFO was prepared each time by following the method of Dzombak and Morel [1]. Briefly, the pH was adjusted by dropwise addition of NaOH to ferric nitrate solution and maintained at a pH of 7.5. HFO was aged about 4-5 h before a metal stock solution with a solid/liquid ratio of 5 g/L was added. For the x-ray absorption fine structure (XAFS) sample preparation, 100-mL suspensions equilibrated for up to 6 mo were collected periodically and centrifuged at 12,900 rpm for 30 min to separate the solid and liquid phase. Supernatants were filtered again by using a 0.2- μ m-pore membrane filter to measure the concentration. The solid part was freeze-dried and stored in a desiccator for the XAFS measurement.

The Zn K edge (9659 eV) XAFS measurements were conducted in fluorescence mode by using a photomultiplier tube (PMT) detector with a bent Laue analyzer [2] at room temperature at Materials Research Collaborative Access Team (MR-CAT) sector 10 or Biophysics CAT (Bio-CAT) sector 18. Data analysis was performed by using the MacXAFS 4.0 program. Fitting was performed by a nonlinear least square fit procedure with a theoretical reference model compound generated

by FEFF8 with WebAtoms 1.4. The samples were fit with the phase and amplitude reference structure of ZnFe₂O₄ to get Zn-O and Zn-Fe relationships.

Results

The radial structure functions (RSFs) of Zn sorbed on HFO are shown in Fig. 1 as a function of reaction time, with aging periods from 1 h to 6 mo. They exhibit similar structures although they have different reaction times. Two predominant peaks are shown in the RSFs for all sorption samples. The first shell corresponds to Zn-O coordination, with the coordination number close to four and a Zn-O distance of \sim 1.96 or 1.97 Å (Table 1). A radial distance of \sim 1.96 Å is a typical value for fourfold coordination of Zn-O [3]. Zn has tetrahedral structure on HFO. The second shell at about 3.44 to 3.47 Å is fitted with about 2.4 to 2.6 Fe atoms (Table 1). There is no evidence of the existence of additional elements or of the formation of mixed-metal coprecipitate or Zn precipitate that contain carbonate, even in systems open to atmospheric CO_{2(g)}. It appears that Zn forms a mononuclear inner-sphere complex on the surface of HFO. Zn sorbed structures on HFO are consistent through different aging periods up to 6 mo.

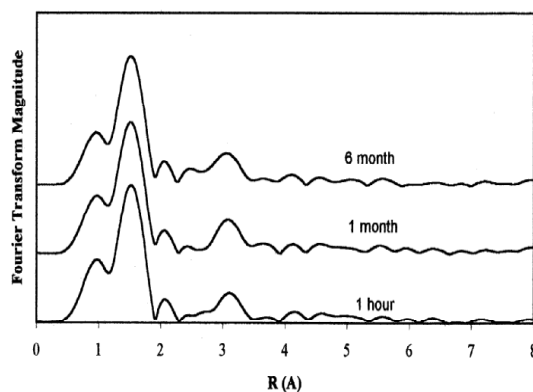


FIG. 1. RSF of Zn sorbed onto HFO obtained by Fourier transformation. These samples were exposed to atmospheric CO_{2(g)}.

Table 1. Extended x-ray absorption fine structure (EXAFS) analysis results of Zn sorbed on HFO.

Sample time	Zn loading (mg/g)	1st shell (O)			2nd shell (Fe)		
		N	R (Å)	σ^2 (Å ²)	N	R (Å)	σ^2 (Å ²)
1 h	11.72	4.1	1.97	0.006	2.4	3.47	0.01
1 mo	12.01	4.4	1.96	0.007	2.6	3.46	0.01
6 mo	12.05	4.0	1.97	0.007	2.6	3.44	0.01

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