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XAFS Study of Cu(II) at the Water-Goethite (α -FeOOH) Interface

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Abstract. Cu(II) complexation at the water-goethite (α -FeOOH) interface was studied by XAFS, potentiometry, and sorption experiments. Thermodynamic data indicate that the initial Cu(II) sorption is not accompanied by release of a H^+ . As pH is raised, hydrolysis occurs, and a maximum of two H^+ are released per sorbed ion. Sorption experiments also show that Cu(II) complexation is insensitive to variation in ionic strength, indicating inner-sphere Cu complexes. The Cu K-edge XAFS suggest that the Cu(II) surface complexes are Jahn-Teller distorted with an equatorial plane of oxygens at approximately 1.95 Å. At pH 5, no 2nd coordination shell is observed. However, at pH 8 there is a well-defined 2nd shell which is best modeled with two Cu atoms at 2.96 Å. The appearance of a 2nd coordination shell at higher pH is attributed to the formation of hydroxo-bridged Cu(II) surface polymers.

1. INTRODUCTION

Chemical reactions at the water-mineral interface influence the fate and transport of transition and heavy metals in surface waters, aquifers, and soils. Iron(III) (hydr)oxides have been recognized as particularly important scavengers of metals ions. In order to understand and to be able to model these system, a detailed knowledge of the interface reactions is needed.

The objective of the present study is to characterize complexes of Cu(II) at the water-goethite (α -FeOOH) interface, both in terms of structure and stoichiometry. This was accomplished by combining thermodynamic methods (potentiometry and sorption experiments) and EXAFS spectroscopy.

2. EXPERIMENTAL

The potentiometric and sorption experiments are described elsewhere [1]. The EXAFS samples were prepared by equilibrating goethite, synthesized according to Atkinson et al. [2], in CO_2 -free 0.1 M $NaNO_3$ solutions containing 0.75 mM $Cu(NO_3)_2$ at pH 5 and 8 for 24 h. Both samples were subsaturated with respect to $Cu(OH)_2$ (s). The samples were centrifuged and the supernatants were analyzed for dissolved Cu. EXAFS data were collected from the remaining wet pastes at SSRL beamline 4-3 at 3.0 GeV beam energy and 50-100 mA current. A Si (220) two-crystal monochromator was used and detuned 50% at 9700 eV. The Cu K-edge spectra were collected in the fluorescence mode using a Canberra array detector. Energy calibration was monitored with a Cu metal foil and an argon-filled ion chamber. Twelve scans were collected for each sample.

The EXAFS spectra were isolated and fit using two different programs: EXAFSPAK (G. George, SSRL) and UWXAFS. In both cases the EXAFS spectra were refined with phase and amplitude functions calculated with FEFF v. 5.04 [3], and the k^3 -weighted spectra were Fourier transformed over the approximate k -range 3-10.5 Å⁻¹. With EXAFSPAK the data were fit in k -space, while UWXAFS was used to fit the R-space data. The agreement was excellent between the values extracted with the two programs; only the results obtained with EXAFSPAK are presented below.

3. RESULTS AND DISCUSSION

The potentiometric and sorption experiments showed that Cu(II) interacts initially with the goethite surface without a release of protons. As pH is raised, however, hydrolysis occurs and a maximum of two protons are released per sorbed Cu(II) ion. It was also found that Cu(II) sorption is insensitive to variation in ionic strength. This indicates that Cu(II) forms inner-sphere surface complexes on goethite.

Results from the quantitative analysis of the Cu K-edge EXAFS data are summarized in Table 1, and the k^3 -weighted EXAFS and the Fourier transforms are presented in Fig. 1. At the goethite surface, Cu(II) is coordinated to oxygen atoms in the 1st shell at 1.94 Å and 1.97 Å in samples pH5 and pH8, respectively. These distances are in good agreement with typical

equatorial Cu-O distances in Jahn-Teller distorted Cu(II) complexes/compounds. This also suggests that the surface complexes are Jahn-Teller distorted, and that the first-shell EXAFS data can be explained by an equatorial plane of oxygen atoms. The deviation from the ideal coordination number 4 in the EXAFS fits (Table 1) can be related to the large uncertainties in the obtained values. Attempts were made to fit two axial oxygens. However, due to the longer distances and higher Debye-Waller factors the presence of axial ligands could not be verified.

Fig. 1. k^3 -weighted EXAFS and Fourier Transforms. The dashed lines are the best fits.

Table 1: Results of the least-squares refinements of the EXAFS

Sample	Atomic pair	N	R (Å)	$\sigma^2(\text{\AA}^2)$
pH5	Cu-O	5.1	1.94	0.0044
pH8	Cu-O	5.1	1.97	0.0049
	Cu-Me	2.1	2.96	0.0097

At pH 5 and 70% coverage of the proton active sites ($= 2.0 \mu\text{mole/m}^2$) no 2nd coordination shell can be detected. The absence of a second shell is unexpected since the sorption experiments indicated formation of inner-sphere complexes, which usually results in a strong contribution from surface Fe back-scattering to the total EXAFS spectrum. Several explanations of this absence are possible.

First, a monodentate linkage between a Jahn-Teller distorted Cu(II) complex and the goethite surface through the axial oxygen would result in an arrangement where a combination of the high Debye-Waller factor of Cu-O_{axial} and the rather long Cu-Fe distance could prevent the detection of the 2nd shell. Another possibility is that a high degree of structural disorder of the surface complexes damps the EXAFS oscillations originating from the 2nd shell. Finally, phase cancellation effects could be the cause of the disappearance of the 2nd shell. However, preliminary FEFF calculations of different possible geometries of the surface complexes suggest that phase cancellation does not occur. We found no evidence of a FT feature at 3.2-3.6 Å which was explained as due to multiple-scattering in an earlier study of Cu(II) in dilute aqueous solutions [4].

In contrast, the pH8 sample (100% surface coverage) shows a well-defined 2nd coordination shell (Fig. 1). This feature is best modeled with approximately two Cu at 2.96 Å. However, because of the similar back-scattering properties of Cu and Fe, the EXAFS data cannot be used to determine conclusively the identity of the 2nd neighbor. There are additional factors that favor Cu over Fe in the 2nd shell. The Cu(II) ion readily forms complexes/compounds where two hydroxide ions bridge two Cu(II) ions in dimers or longer chains, one example being Cu(OH)₂(s). The 2nd-shell structures of such species (Cu-Cu distance in Cu(OH)₂ is 2.95 Å) agree very well with the structure of the pH8 sample which thus might favor Cu as the neighboring ion. Other evidence comes from IR spectroscopy measurements, where we were able to correlate the increased intensity of a Cu-O-H bending band at 1060 cm⁻¹ with the degree of hydrolysis of the adsorbed Cu(II). The frequency of the band suggests that it originates from bridging OH groups. If this is the case, the IR data show that hydroxo-bridged Cu(II) surface polymers form and, consequently, that Cu should be present in 2nd-shell EXAFS data.

To summarize, the insensitivity of sorption to ionic strength indicates that Cu(II) forms inner-sphere surface complexes on goethite. However, due to the absence of Fe back-scattering in the EXAFS data we cannot determine how the complexes are coordinated to the surface. At pH 8, where the solution is subsaturated with respect to Cu(OH)₂(s), hydroxo-bridged polymeric Cu(II) species are most likely formed. This suggests that the hydrolysis of the adsorbed Cu(II) ions, detected in the potentiometric experiments, should be modeled as a polymerization or nucleation reaction and not as hydrolysis of mononuclear surface complexes. Finally, this study shows the importance of combining thermodynamic and spectroscopic investigations to understand surface complexation reactions at solid-water interfaces.

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