

# An EXAFS study of the surface complexation of Zn(II) and Cd(II) at the water-manganite ( $\gamma$ -MnOOH) interface

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Oxides of manganese, iron and aluminum are among the major inorganic compounds, which make up soils. Moreover, they have been recognized as important scavengers of metals and thus attention has been focused on their adsorption properties. Mn is mostly found as Mn(IV) oxides, but it has been shown [1] that at 25°C, the initial solid formed by oxidation of Mn(II) in aqueous solution is a Mn(III) oxide,  $\gamma$ -MnOOH (manganite). In the present work, we investigated the interaction between  $\gamma$ -MnOOH and two heavy metals, Zn(II) and Cd(II), and characterized the surface species by means of EXAFS spectroscopy.

## Experimental

$\gamma$ -MnOOH was synthesised according to Giovanoli and Leuenberger [2], by adding  $H_2O_2$  to a solution of  $MnCl_2$  and  $NH_3$  at 95°C. The solid, characterised by XRD, appeared pure and well-crystallised. TEM observations showed needle-shaped crystals of uniform size. The specific surface area, measured by the BET  $N_2$  adsorption method, was found to be  $30\text{ m}^2\text{ g}^{-1}$ . Sample preparations were performed at 25°C, under argon, by mixing a suspension of  $9\text{ g l}^{-1}$  of solid in 0.1 M  $NaNO_3$  with  $Zn(NO_3)_2$  or  $Cd(NO_3)_2$  solutions, and then adjusting pH with 0.01M NaOH to achieve various surface coverages. Table 1 summarises the samples characteristics. After 30

hours of equilibration time, pH was measured and the samples centrifuged. The supernatant was removed and analysed by AAS for Mn and, Zn or Cd. Adsorption was calculated as the difference between total and measured metal concentrations. The remaining wet paste was mounted under argon in a Teflon cell for XAS experiments. These were performed at SSRL, on beam line 4-1 at 3.0 GeV beam energy, and 50–100 mA current. Zn and Cd K edge spectra were recorded at room temperature in fluorescence mode using a Lytle detector whereas reference samples  $ZnO$ ,  $CdO$ , and  $\beta$ - $Cd(OH)_2$  spectra, were collected in transmission mode. Energy calibration was monitored with the corresponding metal foil.

XAS data analysis was performed using the program EXAFSPAK, and theoretical phase and amplitude functions calculated using Feff7 were used to refine the EXAFS spectra. The distance,  $R$ , the coordination number,  $N$ , and the Debye-Waller factor,  $\sigma^2$ , were optimised, and in no case was the limit on the number of free parameters exceeded. Typical errors for the first shell of atoms surrounding the metal (Zn-O or Cd-O) were  $\pm 0.02\text{ \AA}$  for the distance, and  $\pm 20\%$  for  $N$ . Errors were higher for the second shells,  $\pm 0.04\text{ \AA}$  for the distance. For some samples, the Debye-Waller factor was fixed in the refinement procedure of the second shell, thus increasing the uncertainty on the coordination number.

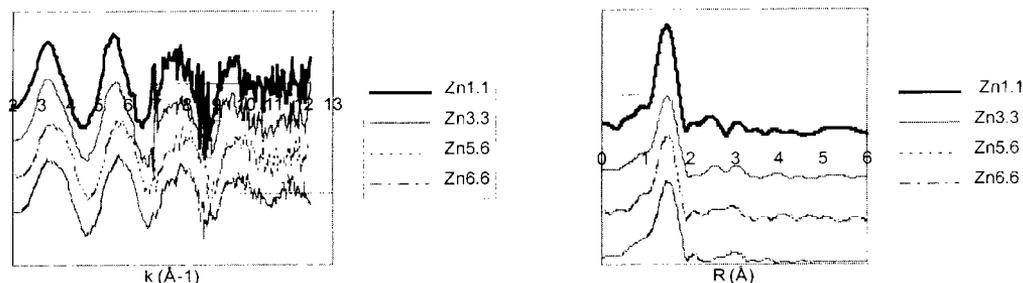


FIG. 1.  $k^3$ -weighted EXAFS and corresponding Fourier Transforms of the Zn samples.

TABLE 1. Sample characteristics

Sample	[Me] <sub>tot</sub> mM	[Me] <sub>equ</sub> mM	% uptake	pH <sub>equ</sub>	Γ mmol/m <sup>2</sup>
Zn1.1	2.574	2.137	11.5	6.27	1.1
Zn3.3	1.695	0.612	58.1	7.09	3.3
Zn5.6	1.695	0.021	98.4	8.20	5.6
Zn6.6	2.574	0.635	68.8	7.43	6.6
Cd2.2	2.273	2.332	24.8	7.37	2.2
Cd3.9	1.538	0.579	62.3	7.95	3.9
Cd4.5	2.133	1.064	50.1	7.91	4.5
Cd6.2	1.454	0.002	100.0	8.72	6.2
Cd6.8	2.010	0.468	76.7	8.35	6.8

## Results

The  $k^3$ -weighted EXAFS and the Fourier Transforms are presented in Fig. 1 for Zn uptake.

In Fig. 1, it is shown that samples with higher coverage show a broadening of the oscillations around  $k = 3.5, 5.5$  and  $10 \text{ \AA}^{-1}$ , which indicates changes in the local structural environment of Zn(II). Fourier transforms of the EXAFS spectra (Fig. 1) are dominated by a first peak at  $1.5 \text{ \AA}$  (uncorrected for phase shift), and a poorly resolved second shell of lower magnitude at  $2\text{--}3.3 \text{ \AA}$ , which is due to more distant backscattering atoms.

An attempt was made to fit the Fourier backtransforms of the first peak with one single shell consisting of oxygen atoms. Poor fits were obtained at low pH, while the fit quality gradually increased with increasing pH. Instead, considering two shells (at about  $1.96 \text{ \AA}$  and  $2.10 \text{ \AA}$ ) greatly improves the fit at low pH. A value of  $1.96 \text{ \AA}$  is typical for Zn(II) in a tetrahedral coordination, whereas a Zn-O distance of  $2.10 \text{ \AA}$  is found for octahedral Zn(II). Thus it appears that Zn(II) switches coordination with pH and so data are best modeled assuming a mixture of  $\text{ZnO}_4$  and  $\text{ZnO}_6$ , the contribution of  $\text{ZnO}_6$  being larger at lower pH.

Higher shells analysis indicates the presence of Mn or Zn at about  $3.08 \text{ \AA}$ , and of Zn at around  $3.30 \text{ \AA}$ . It was not always possible to discriminate between these two metals because of their similar atomic number. Nonetheless, the shortest distance (around  $3.08 \text{ \AA}$ ) was attributed to Mn backscattering, which will be discussed later. When three shells were considered, a better fit was always obtained

considering Mn or Zn in the second shell and Zn in the third shell (at about  $3.3 \text{ \AA}$ ). In this case, assuming Mn in the third shell always resulted in either a much worse fit or a number of neighbours in the second shell unrealistically high ( $N \geq 10$  at  $3.07 \text{ \AA}$ ).

Irrespective of the surface coverage, the Fourier Transforms of the Cd K edge spectra are quite similar. A peak of high magnitude at about  $R = 1.6 \text{ \AA}$  (uncorrected) as well as a low peak around  $2.8 \text{ \AA}$  are always present.

The first shell is best fit with oxygen backscatterers at a distance of  $2.22 \text{ \AA}$ . This distance is constant for all the samples. The number of oxygen atoms is around 6, but a slight decrease with surface loading is detected, and this is probably due to self-absorption of the highly concentrated samples (samples were recorded in fluorescence mode).

The second shell is due to backscattering of Mn at a distance of about  $3.35 \text{ \AA}$ . In this case the shape of the amplitude of the EXAFS of Mn and Cd is very different at low  $k$ , which makes it possible to discriminate between these two atoms in the fitting procedure. No second shell of Cd neighbour was detected in any sample.

## Discussion

Zn(II) and Cd(II), both  $d^{10}$  transition elements, seem to behave rather differently at the surface of manganite.

In the Zn-system, we associate the shortest distance to Mn and so to inner-sphere complexation of Zn(II), as such a short distance between two Zn atoms is not found in any known Zn-hydroxide. The presence of Zn at  $3.30 \text{ \AA}$  is detected for every sample. This suggests that Zn(II) polymerization or precipitation occurs at the surface below the pH of bulk precipitation. The uncertainty in the number of neighbouring atoms,  $N$ , is too high to be able to conclusively decide for precipitation or mixed Mn-Zn hydroxide. Such behaviour for a cation has been reported in several studies, e.g. Co(II) on quartz [3] and, Ni(II) on clays [4].

In the cadmium system, irrespective of the surface coverage, one single second shell of Mn at a constant distance of  $3.35 \text{ \AA}$  is obtained. No Cd is detected which means that cadmium hydroxide precipitation or cluster formation does not occur.

Thus spectroscopic data provide direct evidence that metal ions can behave differently at a water-hydroxide interface.