

**Impact of Fe/Zn Ratios on Zn(II) Species Formed During Co-Precipitation with Ferrihydrite**

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Beamline(s): X11A

**Introduction:** In the mining industry, lime treatment of acidic effluents generates each year large volumes of heavy-metal laden sludges. The Fe/Zn molar ratio of the sludge is highly variable among different metal base industries, ranging from 0.1 to 400. Watzlaf and Casson (1990) observed that a higher ratio of Fe:metal in the sludge was related with lower metal solubility. The objective of this study was to understand the mechanisms of Zn bonding in a system of Zn(II) co-precipitated with poorly-crystalline Fe-oxide at various Fe to Zn molar ratios.

**Methods and Materials:** Samples of Zn(II) formed during the precipitation of ferrihydrite were prepared based on the synthesis procedure for 2-line ferrihydrite (Schwertmann and Cornell, 1991). Ferric solutions containing Zn at Fe/Zn molar ratios of 100, 10, and 1 were precipitated using 1M KOH. The precipitates were washed three times with 1M KNO<sub>3</sub>, and four additional times with DI water, then mounted as freeze-dried powder for XAS analysis. Adsorbed Zn on ferrihydrite (molar ratio of Fe/Zn = 100) was also synthesized and mounted as moist paste for XAS analysis.

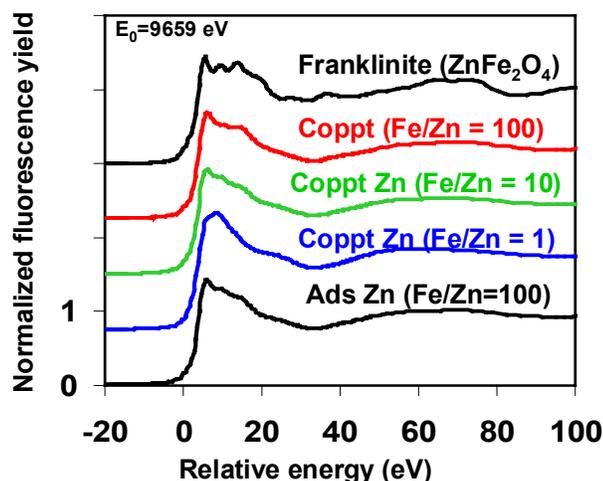
**Results:** Franklinite (ZnFe<sub>2</sub>O<sub>4</sub>) was used as a standard for a mixed Fe/Zn oxide mineral. K-XANES spectra for Fe/Zn=100, Fe/Zn=10 and Zn adsorbed on ferrihydrite were similar to the spectrum from franklinite, showing a shoulder on the high energy side of the white line peak at 15 eV (Fig. 1). As the Zn concentration increased, the shoulder became less pronounced in the Fe/Zn=10 sample and no such shoulder was visible for the Fe/Zn=1 sample. XANES spectra for the Fe/Zn=10 sample looked like the adsorbed Zn species. A significant second shell peak in the radial structure function (RSF) was visible in all samples, except for Fe/Zn = 1 sample (Fig. 2). The magnitude and the radial distance of the second shell peak showed variation among the co-precipitated samples depending on the Fe/Zn molar ratio. The magnitude of the second shell peak was higher in the Fe/Zn = 100 sample than in the Fe/Zn = 10 sample (Fig. 2). The magnitude and the radial distance of the second shell peak for Fe/Zn = 10 sample was similar to that of adsorbed Zn species.

**Conclusions:** XANES and EXAFS data showed that unique species of Zn(II) formed during the precipitation with ferrihydrite, depending on the Fe/Zn ratio. XANES and EXAFS spectra indicated that when ferrihydrite was precipitated from a 10:1 Fe:Zn solution, a significant proportion of Zn (II) was adsorbed. Compared with the Fe/Zn = 10 sample, the higher magnitude of the second shell peak for Fe/Zn = 100 samples suggests that Zn is mostly co-precipitated by isomorphic substitution within the ferrihydrite structure. Structural changes indicated that the limit of isomorphic substitution of Zn (II) for Fe(III) in our samples was between 1% and 10%.

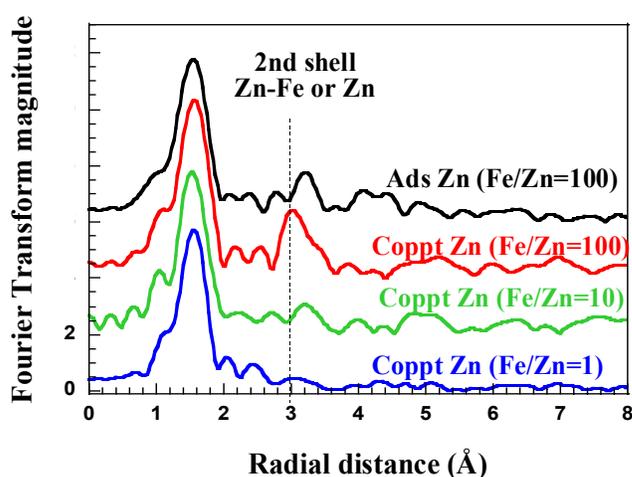
**References:**

Schwertmann, U. and R.M. Cornell, "Iron Oxides in the Laboratory", VCH Publishers, Weinheim, Germany, p. 90-94. 1991.

Watzlaf, G.R. and L.W. Casson, "Chemical stability of manganese and iron in mine drainage treatment sludge: Effects of neutralization chemical, iron concentration, and sludge age", Proc. of 1990 Mining and Reclamation conference and exhibition. Volume 1, pp. 3-9, Charleston, Virginia, USA, 1990.



**Figure 1.** Stacked K-XANES spectra for franklinite, adsorbed Zn and the Zn(II) species formed during precipitation of ferrihydrite at Fe/Zn molar ratios of 100, 10 or 1.



**Figure 2.** Stacked K edge EXAFS spectra (uncorrected for phase shift) for adsorbed Zn and the Zn(II) species formed during precipitation of ferrihydrite at Fe/Zn molar ratios of 100, 10 or 1.