

**Experiment title:**

Micro XANES study of the iron valence state in an iron/corrosion scale/soil system.
Application to the study of the long term corrosion of iron

Experiment number:
ME221

Beamline: ID21	Date of experiment: from: 31.05.01 to: 04.05.01	Date of report: 01.03.02 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Dr. Wolfgang LUDWIG	

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Report:**The following experimental set-up was used :**

Monochromator crystal : Si 220

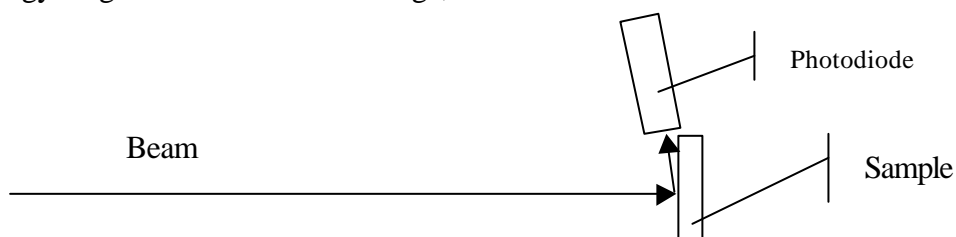
Pinhole : 100 μm , OSA 100 μm

Focusing element : Fresnel Zone Plate

Beam size 2 x 2 μm^2

Detector : Photodiode covered with a Ti foil (5 μm thickness).

Scanned energy range: -100 eV before the edge, +200eV after.

**Reference sample**

In a first step, different reference samples were analysed : magnetite, hematite and goethite. The different prepeaks revealed a good agreement with those already published in literature

Samples

Cross section of the samples were made in order to see the metallic substrate, the different corrosion product layers and the soil.

Analyses

For each sample, a XANES profile was made from the iron substrate to the soil. Depending of the corrosion products thickness, several 10 points per profile were made.

Results

No spectrum showed the shape of a pure iron oxide or oxihydroxide. In the analysed volume, different iron phases were mixed. Thus, to exploit the XANES data and extract the Fe valence and coordination numbers (CN), we used the method published by Galois et al and Wilke et al. These authors analysed plenty of iron containing phases with different valency and CN. In fact, the most useful characteristics of the Fe-K pre-edge for determining Fe oxidation state and CN are the position of its centroid and its integrated intensity.

These values, calculated on the spectra obtained on the reference samples that we analysed (using the peakfit program) were in very good agreement with the results of these authors. That allows us to determine iron valency ($\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio) profiles from the metal to the soil for each analysed samples.

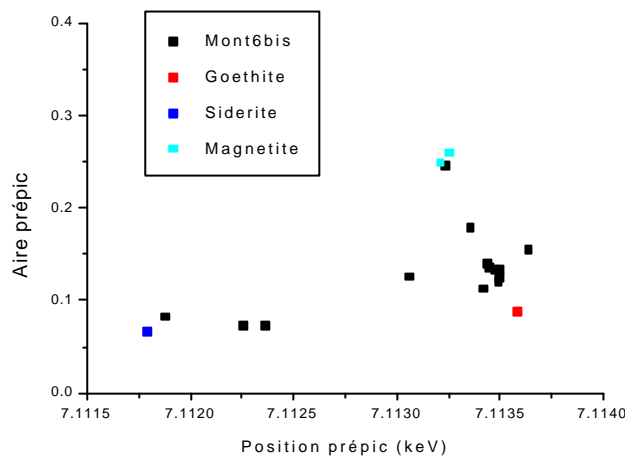


Figure 1 : Prepeak area versus position

Figure 1 shows the prepeak position versus its area for the reference samples (goethite, siderite and magnetite) and for the different points analysed on the corrosion products of a sample; some of these points correspond to a pure Fe^{3+} valency (like goethite) and some other are closer to the Fe^{2+} pole (like siderite)

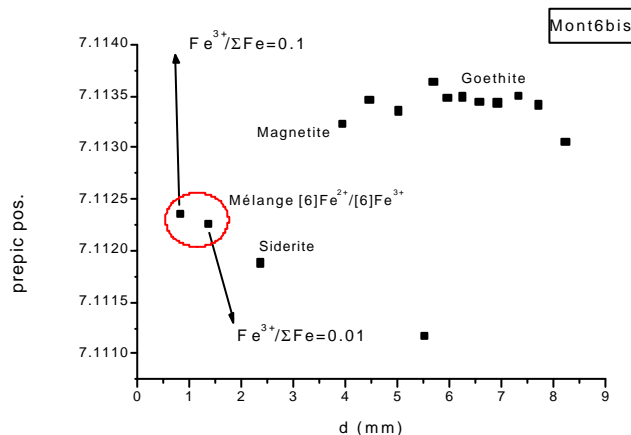


Figure 2 : Prepeak position versus the distance from the metal/oxide interface

It was also possible to determine the prepeak position in function of distance from the metal/oxide interface. Using the data of Wilke, it was possible to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio at different distances from the interface. The more interesting data are far from the interface where the analysed phases are not crystallised and can only be analysed par μXAS techniques.