



Experimental Report

BM30b beamline – proposal n° MA 542

In-situ experiments of reduction of iron and oxides and oxy-hydroxides studied by XAS at the iron K-edge

A) Overview

Atmospheric corrosion of iron is linked to the wet/dry cycles that occur at the iron surface. During the first stage of this cycle, named the wetting stage, the constitutive phases of the rust layer play a role in the corrosion process. Indeed, precedent studies showed that despite of the fact that the corrosion current increases during the wetting stage, the oxygen consumption is negligible. The most common hypothesis in literature is that lepidocrocite (a non conducting iron oxyhydroxide γ -FeOOH) is reducing during this stage in a conducting Fe^{2+} compound, provoking the iron corrosion. Nevertheless, recent studies proves that other high reactive phases as ferrihydrite can be also present in high quantity in the old rust layers and involved in the mechanisms. Because all the long term modelling is based on this strong hypothesis, it is of primary importance to experimentally investigate the kind of phases that forms after reduction.

Because these phases may be unstable, a specific cell (presented in [1-2]) has been designed, to perform *in situ* characterisation during electrochemical experiments. Moreover, as the intermediary phases could be not well crystallised, this cell has been designed to perform XAS experiment.

B) Quality of measurements / data

The Si(220) monochromator enables to get very high quality data for the XANES domain (step 0.3 eV). Moreover, the great stability of FAME beamline ensure good quality signal over the whole EXAFS domain k [0-15 \AA^{-1}]. Finally, the beamline environment was very practical for our cell, and despite the large number of instruments we had to install, no problems were encountered.

C) Results

1. Reduction experiments

Two reference phases, the active lepidocrocite and the potentially active 2-line ferrihydrite have been reduced in the electrochemical cell, with two different solutions at pH = 7.5 (PIPES buffer) and pH = 9 (TAPS buffer). EXAFS spectra at the Fe K edge have been collected before and after the reduction process, whereas only the XANES domain was investigated during the reduction of the phases and the formation of the new compound. Thanks to the FAME beamline geometry, all acquisitions could be carried out in the transmission mode.

The reduction at pH = 7.5 and 9 on lepidocrocite and ferrihydrite give very interesting results. The figures 1 and 2 present an example of the reduction of ferrihydrite at pH = 7.5. An edge shift is clearly observed during the reduction process (figure 1), confirming the decrease of the oxidation state. Moreover, the comparison of the initial and final EXAFS spectra demonstrates a good agreement with the formation of magnetite (figure 2).

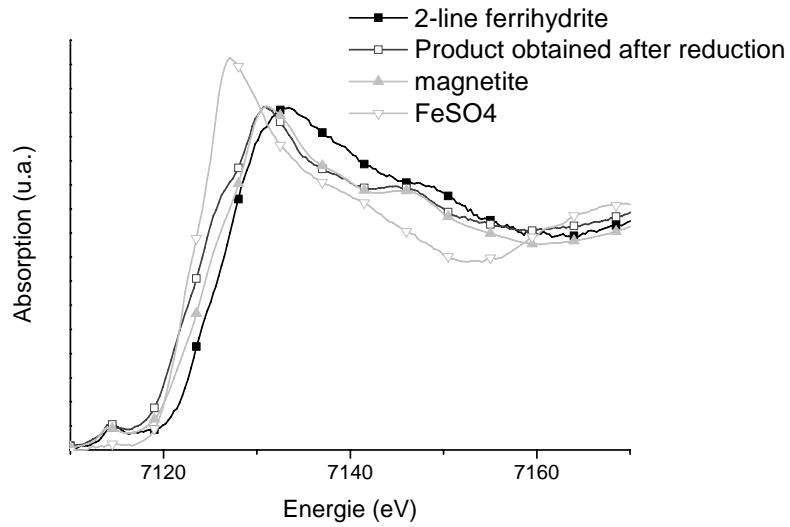


Figure 1 : XANES spectra recorded during the reduction process of 2-line ferrihydrite at pH = 7.5. Comparison with magnetite (intermediate Fe^{II}/Fe^{III} phase) and iron sulphate (Fe^{II} phase).

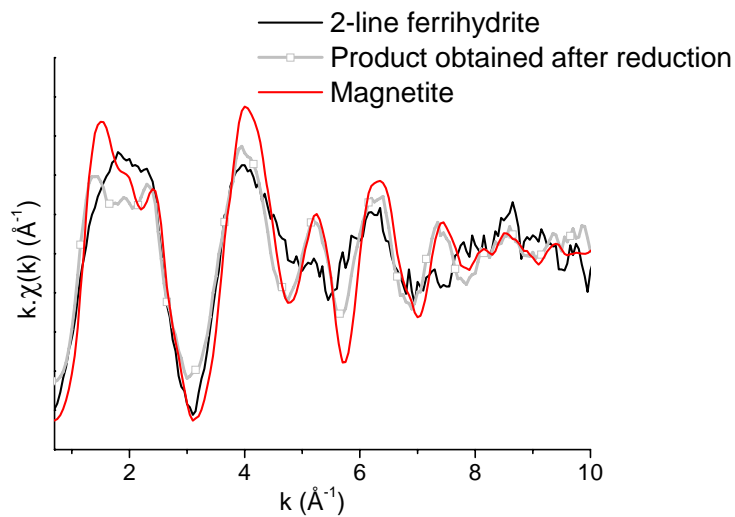


Figure 2 : Initial EXAFS spectra of 2-line ferrihydrite before the reduction and EXAFS spectra of the phase obtained after reduction at pH = 7.5. Comparison with the magnetite EXAFS spectra

When the reduction was undertaken at pH = 9, another EXAFS spectra was identified. The final product is a Fe^{II} phase that could be iron hydroxide Fe(OH)₂.

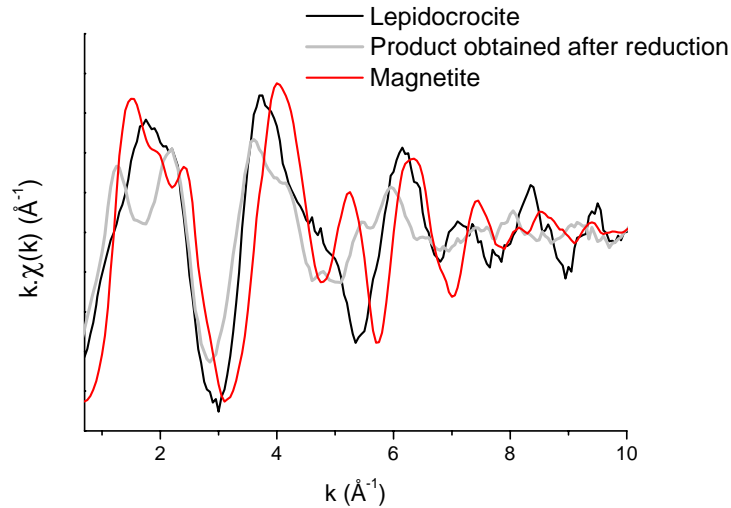


Figure 3 : Initial EXAFS spectra of lepidocrocite before the reduction and EXAFS spectra of the phase obtained after reduction at pH = 9. Comparison with the magnetite EXAFS spectra to show the disagreement between final and magnetite phases.

The table 1 presents a summary of the obtained results. It is clearly shown that the nature of the initial phase has no influence on the nature of the reduced phase. On the contrary, the pH seems to strongly influence the nature of the reduced phase

Table 1: Results obtained through reduction experiments followed with XAS (imposed potential -1E/SCE, NaCl 0,1 mol.L⁻¹, pH = 7.5 or 9 with buffer PIPES or TAPS)

pH/E(V/SCE)	pH = 7.5 -1 V/SCE	pH = 9 -1 V/SCE
Lepidocrocite	Fe ₃ O ₄	Mainly Fe(OH) ₂ + Fe ₃ O ₄
2-line ferrihydrite	Fe ₃ O ₄ + ε Fe(OH) ₂	Fe(OH) ₂ + ε Fe ₃ O ₄

D) Status and progress of evaluation.

This experiment on reference phases reveals the great potential of the FAME beamline to understand the reduction process occurring during the wetting and the drying of iron samples. Moreover, the identification of magnetite and iron hydroxide, two conductive phases, hold some interesting hypothesis on the corrosion mechanisms in the following of the cycle. To go further, it would be very interesting to study the whole cycle that mean both reduction and reoxydation processes. Moreover, after the study on reference phases, the further step to better understand iron corrosion mechanisms could be to study following the same principle the reduction of corrosion product powder scratched on the surface of corroded samples.

E) Bibliography

- [1] J. Monnier *et al.* Journal of Nuclear Materials 379 (2008) pp 105-111
- [2] J. Monnier. Corrosion atmosphérique sous abri d'alliages ferreux historiques. Caractérisation du système, mécanismes et apport à la modélisation. Paris-Est University, 2008, 299 pages. Downloadable on the URL : <http://tel.archives-ouvertes.fr/tel-00369510/fr/>.