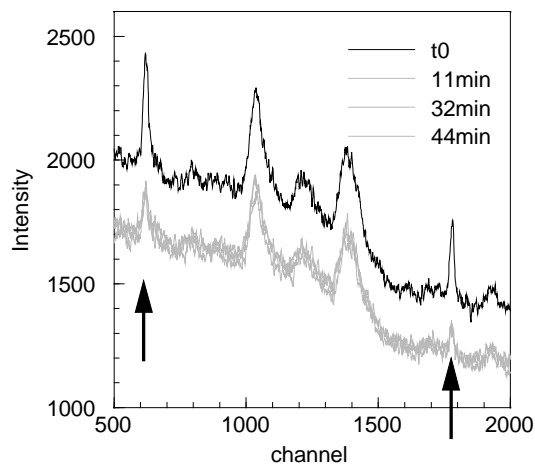
	Experiment title: Mechanism of the reductive dissolution of iron oxides by sulfide	Experiment number: 26-01-864
	Beamline: BM26	Date of experiment: from: 30/10/09 to: 03/11/09
Shifts: 15	Local contact(s): Dr Sergey Nikitenko	Date of report: 26/03/2010
<i>Received at ESRF:</i>		
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Technical aspects: The purpose of the experiment was to follow the reaction of iron oxides suspensions with S(-II) on line by using WAXS and XAFS. For this purpose a batch reactor set-up was installed in the experimental hutch. For performing WAXS and XAFS measurements a part of the experimental suspension was circulated through a capillary which was installed in the beam. The batch reactor was equipped with a pH stat device and a syringe pump for adding a Na₂S solution. The whole set-up was modified in a way that it was possible to control the different components (peristaltic pump, syringe pump, and the pH-stat device) remotely from the control cabin.

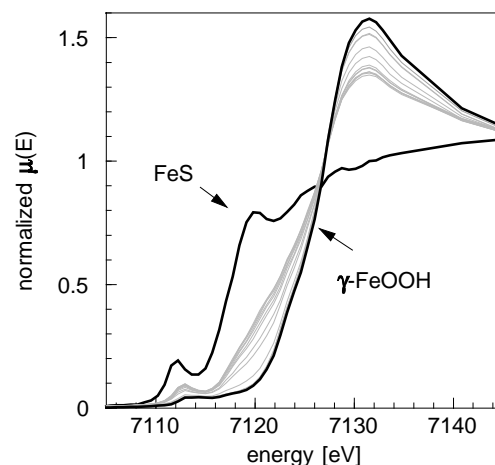
A challenge in the preparation of the experiments was to adjust the experimental design in a way that XAFS and WAXS measurements can be performed within the limits of controlling the chemical reaction itself. First of all, the time scale of the reaction progress had to be optimized by varying the experimental conditions so that it was possible to follow the reaction on-line within the limits of the allocated beamtime and the required time frame for collecting high quality spectra and diffractogram. This optimization was constrained by the a) required jump height and b) the maximum X-ray absorption by the capillary containing the experimental suspension, for collecting XAFS spectra. For this purpose, following parameters had to be coherently optimized: diameter and material of the capillary, iron oxide concentration, and the required amounts of acid and S(-II) solution for driving the reactions. In this context, I would like to mention the excellent support by Dr Sergey Nikitenko during the performance of the experiment, but particularly during the preparation of the experiment. He answered all our questions immediately and helped us enormously regarding the technical aspects of performing the experiment. Thanks to his support it has been possible to optimally use the allocated beamtime. Directly from the start of the experiment we obtained excellent results and no further adjustment of the experimental conditions had to be performed. This outcome was above our expectations and throughout the whole experiment the collection of XAFS and WAXS data went without any problems. The only technical problem we faced was clogging of the capillary which occurred unexpectedly in the experiments with the highest amounts of added S(-II). In total 8 on-line experiments were performed in which S(-II) concentrations (between 12.5 and 100% of the stoichiometrically required amount to completely transfer FeOOH into FeS) and pH were varied (7-9). In the first stage of the experiment, a sequence consisting of the subsequent collection of WAXS, XANES, and qEXAFS data was continuously repeated until the acid consumption ceased and indicated the completion of the reactions. Afterwards, EXAFS spectra collection was alternated with WAXS analysis.

Scientific aspects:

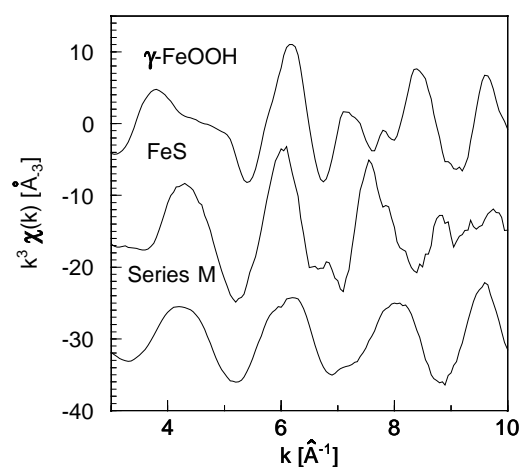
The reductive dissolution of the lepidocrocite (FeOOH) was reflected in the diminishing of the characteristic peaks in the diffractogram (right figure, arrows mark characteristic diffraction peaks of lepidocrocite). No formation of materials with sufficient long range order to create diffraction peaks was observed. In contrast to our previous experiments we did not observe that the diffraction peaks of lepidocrocite re-appeared after aging of the suspension for more than 24h. Interestingly, the change in the diffractograms occurred within the first 11 min of the experiment and afterwards no further significant changes were observed.



The progress of the reaction was also followed by the change in the XANES spectra Fe-K edge (right figure, the black lines are lepidocrocite and FeS, respectively). The shape of the XANES spectra can be well reproduced by a linear combination of the spectra of lepidocrocite and FeS, which was synthesized by adding S(-II) solution to Fe^{2+} solution in the reactor vessel. The time evolution of the spectra can be used to infer the kinetics of the reaction. For this purpose the decrease in the relative contribution of the lepidocrocite spectrum in the linear combination fit was used. As expected, the reaction proceeded slower at pH 9 than at pH 8 and pH 7. The amount of sulfide, however, seemed not to have an effect on the rates of the reaction at pH 8. An interesting observation was that the change in XRD spectra occurred typically faster than the change in XANES spectra.



While all XANES spectra can be satisfactorily explained by using the combination of two end members, ITFA analysis¹ of the EXAFS spectra revealed, that two components are insufficient to describe all the EXAFS spectra. An important finding is that the product of the reaction of S(-II) with lepidocrocite is not identical with the FeS obtained by combining Fe^{2+} and S(-II) solution. This is exemplarily shown in the right figure. In series M the highest amount of S(-II) has been added. According to the XANES spectrum more than 75% of the initial lepidocrocite has reacted at the end of the experiment. However, the EXAFS spectrum is significantly different to that of FeS and cannot be reproduced by combining the EXAFS spectra from FeS and lepidocrocite. Preliminary fitting of the spectra indicates that the closest Fe-Fe shells of lepidocrocite are still present in the product. This supports our hypothesis that the short range coordination environment of lepidocrocite is partially maintained in the product and that the reaction mechanism is different than generally believed.



¹ Rossberg A., Reich T., and Bernhard G. (2003) Complexation of uranium(VI) with protocatechuic acid-application of iterative transformation factor analysis to EXAFS spectroscopy. *Analytical and Bioanalytical Chemistry* **376**(5), 631-638.