



DUBBLE – EXPERIMENT REPORT

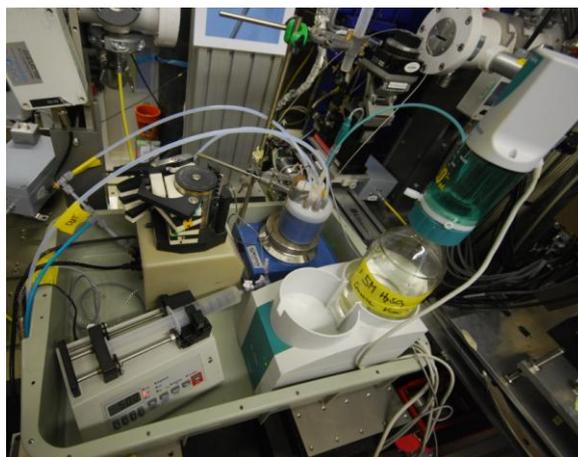
We kindly request you to answer the questions (max 2 pages) and return the form to NWO **within 2 months of the completion of the experiment** to dubble@nwo.nl

Beam time number: 26-01-897		File number:
Beamline: BM 26A	Date(s) of experiment: 16/2-20/2/2011	Date of report: 30/4/2011
Shifts: 12	Local contact(s): Miguel Silveira, Segey Nikitenko	

- 1. Who took part in the experiments?** (Please indicate names and affiliations)
At ESRF: Dr. Miguel Silveira (KU Leuven, DUBBLE), Dr. Thilo Behrends, Bas Vriens, Okke Merckx (Earth Sciences, Utrecht University)
- 2. Were you able to execute the planned experiments?**
YES
- 3. Did you encounter experimental problems?**
No, but the inhomogeneous distribution of the solids in the capillary caused problems when collecting EXAFS spectra due to the offset of the beam. Furthermore, the data acquisition program frequently crashed and therefore continuous supervision was required and some spectra were lost.
- 4. Was the local support adequate?**
YES, perfect
- 5. Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?**
YES
- 6. Are you planning follow-up experiments at DUBBLE for this project?**
YES
- 7. Are you planning experiments at other synchrotrons in the near future?**
NO
- 8. Do you expect any scientific output from this experimental session (publication, patent, ...)**
YES, until end 2011
- 9. Additional remarks**

Technical aspects

The reaction of several Mn oxides with sulfide was performed in batch reactors at different pH. Additionally the amount of added S(-II) was varied. The pH was kept constant with an automatic pH stat device. The reaction was initiated by adding S(-II) solution to Mn oxide suspension by using a syringe pump. For measuring WAXS and collecting XAS spectra, the suspension was pumped through a PEEK capillary with a peristaltic pump. The capillary was located in the beam. X-ray scattering was detected with an INEL detector, while XAS spectra were collected in transmission mode.



It was possible to control the peristaltic pump, the syringe pump, and the pH stat device from the control cabin so that manipulation were possible without interrupting the data acquisition. The experimental set-up worked without any problems. Despite all attempts to vary the length of the capillary, the pumping velocity of the peristaltic pump, or the stirring speed in the reactor, we did not succeed to realize a homogeneous distribution of the suspension in the capillary. As a consequence, optimizing the vertical position of the beam turned out to be crucial for obtaining XAS spectra of good quality. Nevertheless, the vertical concentration profile of the suspensions in the capillary changed during the reaction. This problem was aggravated by the offset of the beam during EXAFS measurements, leading to highly concave or convex backgrounds. The latter complicated finding a consistent procedure for normalizing the spectra and removing the background for EXAFS analysis.

Results

The homogeneity of the suspensions in the capillary varied between the different Mn oxides so that most of the experiments were performed with one pyrolusite (MnO_2) material which caused the least problems. In total, six experiments were performed on line. In the first hours after S(-II) addition, the progress of the reaction was fast, and WAXS, XANES, and q-EXAFS data were sequentially collected. The collection of data for one sequence took about 15 minute. Afterwards, the reaction slowed down, so that the collection of EXAFS spectra was possible without significant changes in the system during the acquisition time.

The WAXS signal from the suspensions in the capillary was relatively weak and long periods of data collection would have been required to obtain acceptable signal to noise ratios. In view of the rates of the reaction and the higher relevance of information from XANES and q-EXAFS spectra, we accepted that WAXS data were of relatively low quality. The energy correction of q-EXAFS data was performed by aligning q-EXAFS spectra to XANES spectra collected directly before the q-EXAFS measurements.

The reduction of MnO_2 upon addition of S(-II) and the transformation of Mn-oxides into Mn-sulfides was reflected in the change of XAS spectra (Fig.1). Principal component analysis was performed on the XANES part of the q-EXAFS, XANES, and EXAFS spectra by using the ITFA software (Rossberg et al., 2006). Principal component analysis (PCA) revealed that two components were sufficient to account for the majority of the variance in all the spectra. One component can be related to the Mn spectrum of the initially added pyrolusite. The second component was highly loaded by the spectrum of precipitate rose MnS which was formed by adding S(-II) solution to Mn(II) solution in the batch reactor. Hence, the change in XANES

spectra can be interpreted as the transformation of pyrolusite into MnS upon the reaction of S(-II) with MnO₂.

The results from PCA analysis imply that the reduction of Mn(IV) by S(-II) occurs via a two electron step and no intermediate Mn(III) is formed. When using the spectra of pyrolusite and MnS to constrain the endmembers in the iterative target test of the ITFA program, the relative contribution of the two components to the different spectra is obtained. In Fig. 2 these relative concentrations are multiplied by the amount of Mn (0.1 mol) in the system and are presented as concentrations of MnO₂ and MnS. Based on this analysis, the rates of the transformation MnO₂ into MnS can be derived and compared to the rates of acid addition during the experiment. Several interesting observations can be made which will not be discussed here in detail:

1) The transformation of MnO₂ into MnS occurs in two phases, a fast initial phase and a slower second phase in which the transformation proceeds almost linearly with time
 2) the extent of MnO₂ transformation during the first phase depends on pH and decreases with increasing pH
 3) the ratio between acid consumption and MnO₂ transformation deviates from the ratio expected from the proposed stoichiometry of the reaction, the deviation is most emphasized at pH 9.5.

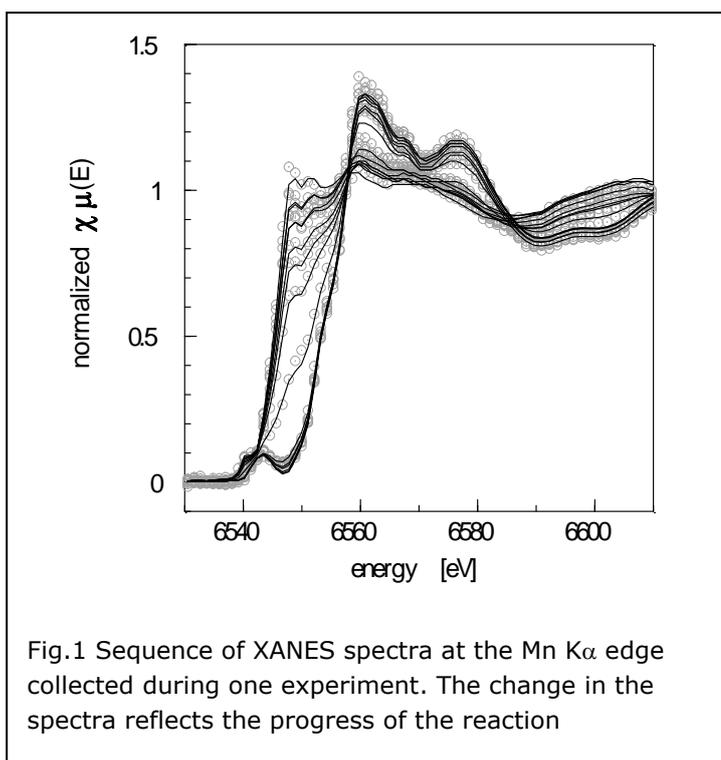


Fig.1 Sequence of XANES spectra at the Mn K α edge collected during one experiment. The change in the spectra reflects the progress of the reaction

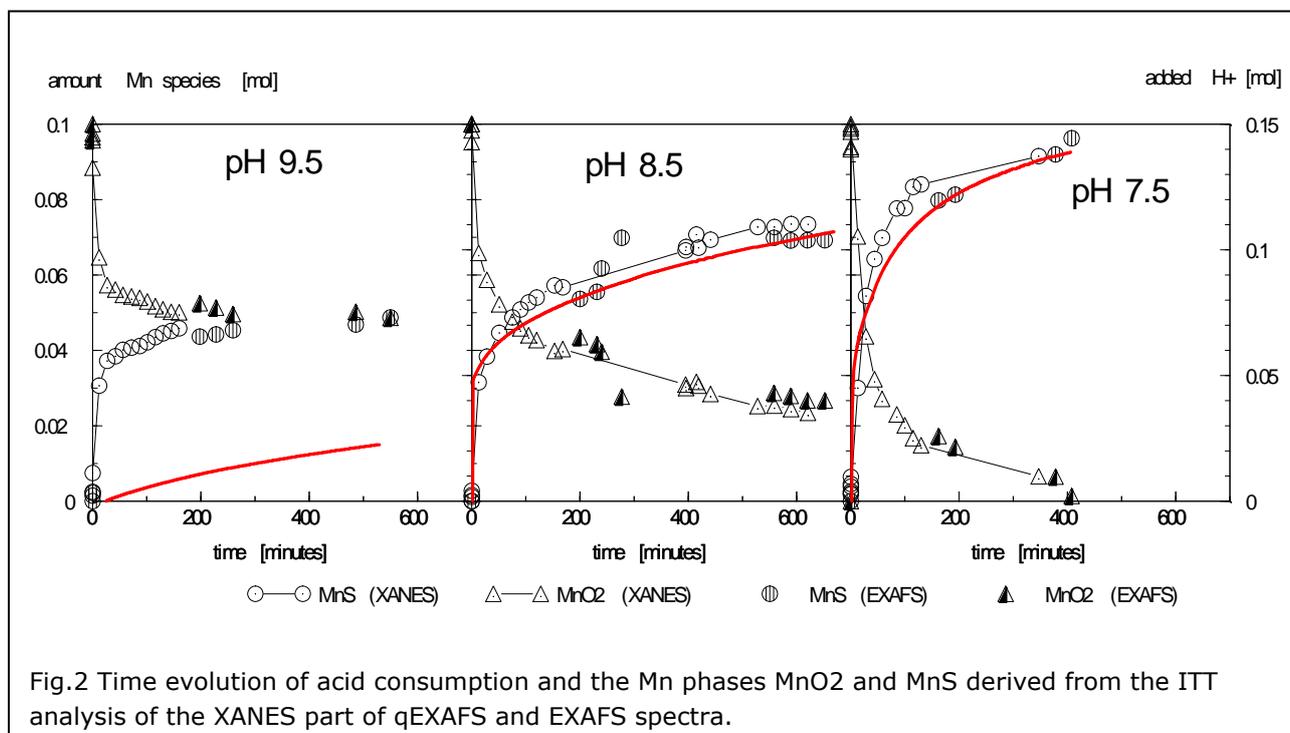


Fig.2 Time evolution of acid consumption and the Mn phases MnO₂ and MnS derived from the ITT analysis of the XANES part of qEXAFS and EXAFS spectra.

The preliminary analysis of the EXAFS spectra indicates that the structure of MnS formed during the reaction with MnO₂ is similar to that of precipitated rose MnS formed by adding S(-II) solution to Mn(II) solution. The EXAFS spectrum of rose MnS differs significantly to that of green MnS which has alabandite structure.

Literature

Rosberg, A., Reich, T. & Bernhard, G. (2003). Analytical and Bioanalytical Chemistry 376, 631-638



DUBBLE - CLAIM FORM FOR COSTS OF TRAVEL/SUBSISTENCE

Dutch users of beam time at DUBBLE can use this form to claim full/partial reimbursement of the associated costs of travel and subsistence. The form must be returned to NWO **within 2 months of the completion of the experiment** to dubble@nwo.nl

Reimbursement rules (costs are reimbursed to the Main Proposer)

Travel costs

€ 400 p.p. for max. 3 persons.

Subsistence costs

Subsistence costs are reimbursed for max. 3 persons @ € 60 p.p. per day (incl. 1 day before and 1 day after the experiment).

Applicant (Main Proposer) : ___Thilo Behrends___

Beam time number : 26-01-897___

Experiment dates : __16 -20 February 2011_____

Participants (max 3 persons):

Name : ___Thilo Behrends___ 400 + 6*60 = 760 Euro

Name : ___Bas Vriens___ 400 + 6*60 = 760 Euro

Name : ___Okke Merkx___ 400 + 6*60 = 760 Euro ___

Payment details

Pay to account no.: _____ 8335272_____

Name: _____Thilo Behrends_____

City: ___IJsselstein___