



**DUTCH-BELGIAN BEAMLINE
AT ESRF**

**EUROPEAN
SYNCHROTRON
RADIATION FACILITY**




Experiment Report Form

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

(next page)



| | | |
|---|--|---|
|  | Experiment title: Investigation of biogenic MnO _x formed at the long term sorption of Mn(II) by <i>Shewanella putrefaciens</i> . | Experiment number: 26-01-794 |
| Beamline: BM26A | Date(s) of experiment: From: 21-09-2007 To: 25-09-2007 | Date of report: 31-10-2007 |
| Shifts: 12 | Local contact(s): Dr. Sergey NIKITENKO | |
| Names and affiliations of applicants (* indicates experimentalists): Natalia Chubar, Mihaela-Cristina Avramut. Department of Earth Sciences - Geochemistry, Faculty of Geosciences, Utrecht University, P.O. Box 80.021, 3508 TA Utrecht, The Netherlands | | |

Report: (max. 2 pages)

Part of the recent research of the applicants was devoted to adsorption studies of Mn²⁺ by *Shewanella putrefaciens* in batch conditions (pH effect, kinetics of adsorption, equilibrium isotherms, the effect of the bacteria doses on adsorption). Discovered particularity of the surface chemical properties and sorptive behavior of living microorganisms towards Mn²⁺ encouraged us to run sorption studies for longer time (over 30 days) and at different temperatures (5, 10, 22 and 30 °C) as well as at the different initial concentrations of Mn²⁺. Long term studies of Mn sorption by living *Shewanella putrefaciens* demonstrated that beside ion exchange and complexation there are few other processes taking place at the interface of bacteria and metal ions. FTIR spectroscopy allowed concluding about oxidation of Mn²⁺ taking place during sorption by live *Shewanella p.* FTIR spectra suggested that oxidation did not take place at the lower temperatures (5 °C), and the rate of oxidation was also dependent on the bacteria content (dose) and the initial concentration of Mn²⁺.

Full X-ray absorption spectra (comprising XANES and EXAFS) were collected for the samples and reference materials. It let is to confirm conclusions drawn from FTIR spectra, e.g. that oxidation of Mn²⁺ takes place during long term contact of Mn²⁺ by Mn-reducing bacteria *Shewanella putrefaciens*. This process of oxidation depends on the concentration of the initial ions of Mn(II), on the contact time of Mn²⁺ and bacterial suspensions, on the concentration of bacteria in the experimental solutions (e.g. 2 or 4 g of dry weight per liter) and the temperature. Absence of Mn²⁺ oxidation at the temperature of 5 °C was also confirmed. Moreover, EXAFS and XANES investigation allowed finding out what kind of bonding take place at this temperature for longer period of bacteria contact with Mn²⁺ and what kind of compounds formed at the absence of oxidation. Detailed explanation of the scientific information obtained from XANES and EXAFS spectra will be shown in the paper. Using the results obtained in the framework of the NWO project for Dutch-Belgian beamline at the ESRF, in combination with previous FTIR characterization of Mn-containing bio-precipitates formed by *Shewanella putrefaciens*, the following manuscript is under preparation and will be submitted in due time as soon as possible:

N. Chubar, M. C. Avramut, T. Visser, T. Behrends, P. van Cappellen. EXAFS, XANES and FTIR studies of the precipitates formed by *Shewanella putrefaciens* at the contact with Mn²⁺ at different temperatures.

We will provide a copy of the manuscript as soon as it will be accepted and send the reference about it to ESRF as soon as it will be published.

19 samples from the experiments described above and 10 reference materials were studied at the ESRF for the period of September 20-25, 2007. Taking into account that biogenically formed precipitates can have different or mixed composition as previously was shown in the literature, we obtained XANES and EXAFS

spectra for **10 reference materials**:

1) MnO, 2) MnO₂ , powder, 3) MnO₂ pyrolusite 4) MnO(OH) (manganite) , 5) Mn₃O₄ , 6) Mn₂O₃ 7) MnPO₄ 8) MnCO₃ 9) MnCl₂ 10) MnSO₄.

19 samples (№ 1-19 as shown in the Table below) from adsorption studies of Mn²⁺ by living *Shewanella putrefaciens* were chosen as the following:

| № | Mn ²⁺ concentration | Temperature | Contact time | № | Mn ²⁺ concentration | Temperature | Contact time |
|----|-----------------------------------|-------------------------|-----------------|----|-----------------------------------|-------------------------|--------------|
| 1 | 200 mg/L | 5 °C | 30 days | 11 | 400 mg/L | 22±2 °C (room temp.) | 14 days |
| 2 | 200 mg/L | 10 °C | 30 days | 12 | 750 mg/L | 22±2 °C (room temp.) | 3 days |
| 3 | 200 mg/L | 22±2 °C (room temp.) | 9 days | 13 | 750 mg/L | 22±2 °C (room temp.) | 16 days |
| 4 | 200 mg/L | 22±2 °C (room temp.) | 30 days | 14 | 750 mg/L | 22±2 °C (room temp.) | 22 days |
| 5 | 200 mg/L | 30 °C | 6 days | 15 | 750 mg/L | 22±2 °C (room temp.) | 24 days |
| 6 | 200 mg/L | 30 °C | 10 days | 16 | 1000 mg/L | 22±2 °C (room temp.) | 4 days |
| 7 | No Mn(II) Just bacteria | Room temp. | 30 days | 17 | 1000 mg/L | 22±2 °C (room temp.) | 6 days |
| 8 | 125 mg/L | 22±2 °C (room temp.) | 9 days | 18 | 1000 mg/L | 22±2 °C (room temp.) | 12 days |
| 9 | 125 mg/L | 22±2 °C (room temp.) | 16 days | 19 | 1000 mg/L | 22±2 °C (room temp.) | 19 days |
| 10 | 125 mg/L | 22±2 °C (room temp.) | 30 days | | | | |

We thank to Dr. Sergey Nikitenko for technical support of our work at the BM26A what allowed us to obtain the spectra of high quality as well as for his cooperative attitude supporting us during weekend, when needed, what allowed us to study so many samples during our first time work at the European Synchrotron Radiation Facility. We also thank to Dr. Wim Bras for his cooperative support of our research at the ESRF.