EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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.

ESRF	**Experiment title: Characterization of Fe(III)-precipitates forming in aerated As(III)- and Fe(II)-containing groundwater and implications for As-removal from**	**Experiment number**: 01-01-813
Beamline:	**Date of experiment**: from: 23.9.2009 to: 28.9.2009	**Date of report**: 28.2.2010
Shifts:	**Local contact(s)**: Sergey Nikitenko	*Received at ESRF:*

Names and affiliations of applicants:

Dr. Andreas Voegelin, Eawag, Switzerland

Dr. Ralf Kaegi, Eawag, Switzerland

Dr. Stephan Hug, Eawag, Switzerland

Experimenters:

Dr. Andreas Voegelin, Eawag, Switzerland

Beate Fulda, ETH Zurich, Switzerland

Report: ***Ag speciation in wastewater and wastewater treatment sludge***

Due to a mismatch between the timing of beamtime allocation and experimental work, we could not perform the proposed study. Instead, we used the beamtime at DUBBLE for a pilot study to determine the potential of XAS for the speciation of Ag in sewer systems.

Silver nanoparticles (Ag-NP) are used in a wide range of products because of their antimicrobial properties. The amounts of Ag-NP used are rapidly increasing, but little is known about their environmental impact. From most applications, Ag-NP are emitted into sewer systems. Therefore, the retention of Ag-NP in wastewater treatment plants (WWTP) is a critical factor controlling the potential exposure of environmental systems to Ag-NP and their transformation products. Thus, in order to assess potential environmental risks associated with the increasing use of Ag-NP, the processes controllling their retention and transformation in WWTP must be understood. In this context, information on Ag speciation is essential.

We performed a preliminary study to investigate the potential use of Ag K-edge XAS for determining Ag speciation in wastewater and sewage sludge focusing on two systems:

1) Speciation of Ag emitted from an industrial laundry using AgCl at three locations: Laundry effluent (~500 µg/L Ag), WWTP influent (~5 µg/L Ag) and WWTP sludge (~45 mg/kg Ag).

2) Speciation of activated sewage sludge from a pilot WWTP run with Ag-NP-spiked wastewater (~1500 mg/kg Ag-NP in sludge).

The Ag K-edge XANES and EXAFS spectra of these samples were recorded at room temperature in fluorescence mode at the DUBBLE beamline. For the interpretation of experimental spectra by linear combination fitting, a series of reference materials were analyzed (in transmission mode), amongst others metallic Ag, Ag-NP, AgCl, Ag_2S, Ag_2O, thiol-bound Ag^+, Ag-lactate, and aqueous Ag^+. Reference spectra and experimental spectra are shown in Fig. 1 and results from the analysis of experimental XANES and EXAFS spectra by linear combination fitting are given in Table 1.

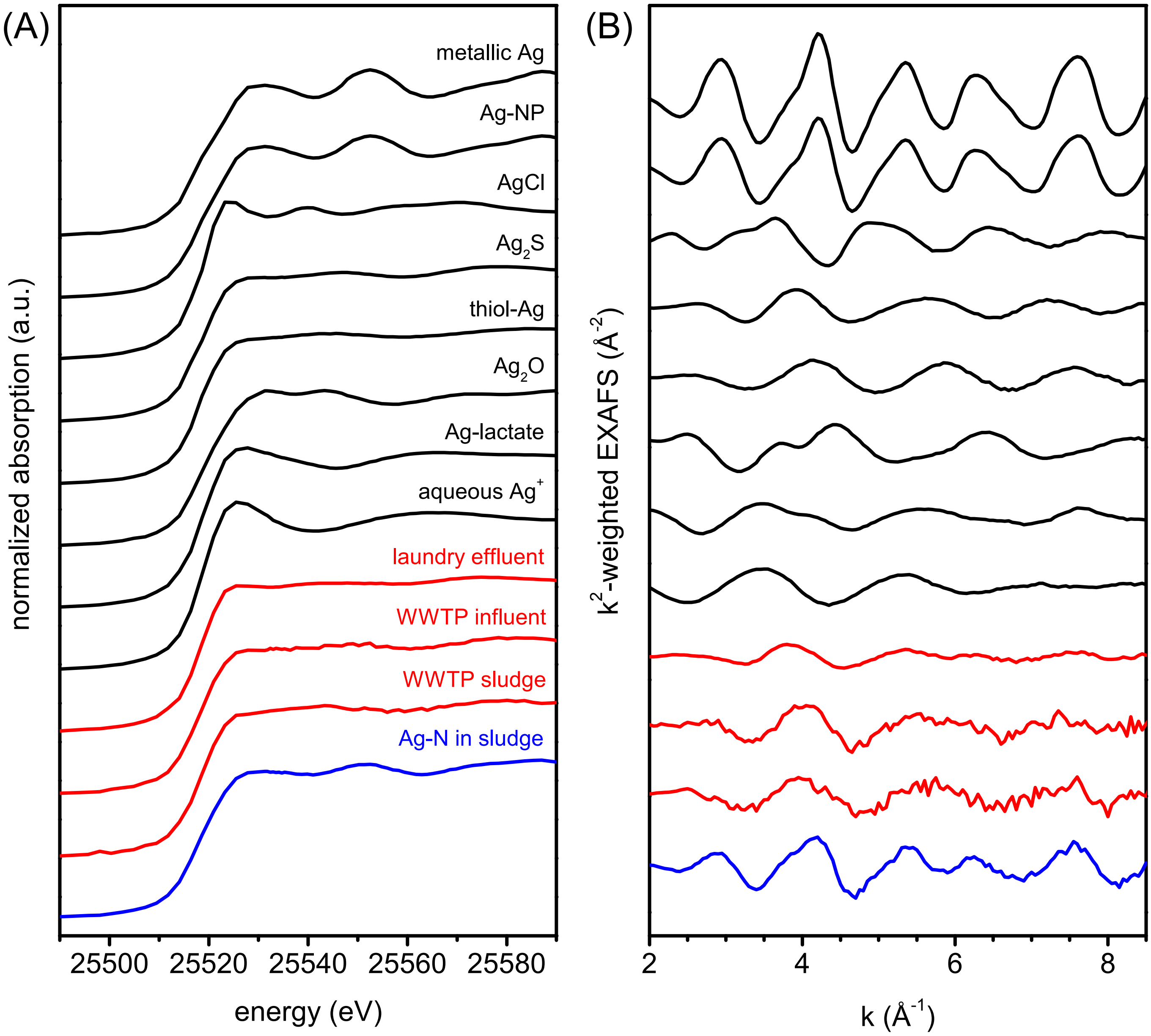

Fig. 1. Ag K-edge XANES (A) and EXAFS (B) spectra of reference compounds and of wastewater and sewage sludge samples.

Reference spectra of metallic Ag, sulfur-coordinated Ag and oxygen-coordinated Ag produced clearly distinguishable spectra both in the XANES and EXAFS region (Fig. 1). Linear combination fitting of the experimental spectra with the five most suitable reference spectra returned similar results for the XANES and EXAFS region (Table 1, Ag_2O was included as proxy for oxygen-coordinated Ag). In the laundry effluent, AgCl used in the washing process was still detected but most Ag was sulfur-bound, either by complexation with thiol groups or as Ag_2S. Sulfur-coordination further increased towards the WWTP influent and dominated Ag speciation in the WWTP sludge. In the case of the pilot WWTP plant running with Ag-NP treated wastewater, about 50% of the metallic Ag-NP had transformed into sulfur-coordinated Ag within the sludge (Table 1). These first results emphasize that Ag undergoes substantial changes in speciation within sewer systems, with sulfur-coordination playing a major role. The data further demonstrated the possibility of speciating particulate Ag in water at concentrations as low as 5 µg/L (after pre-concentration of the particulate phase on filter membranes). With respect to Ag-coordination with sulfur, distinction between thiol-bound Ag^+ and Ag_2S is not always unequivocal. Distinction between these species however could be improved by measuring spectra at 77K rather than at room temperature.

Table 1. Linear combination fit results for experimental XANES (top row) and EXAFS (bottom row) spectra based on five most relevant reference spectra (XANES: -50 to 150 eV around edge; EXAFS: 3 to 8 Å^{-1}).

	metallic Ag	AgCl	Ag_2S	thiol-Ag	Ag_2O	sum
	(%)					
	1) Speciation of Ag emitted from an industrial laundry using AgCl					
laundry effluent	—	36	36	32	—	104
	7	36	45	19	—	108
WWTP influent	10	—	70	20	—	100
	15	—	86	13	—	114
WWTP sludge	—	—	61	39	—	100
	—	—	78	34	—	112
	2) Activated sludge from a pilot WWTP run with Ag-NP-spiked wastewater					
Ag-NP in sludge	44	—	47	10	—	101
	50	—	57	10	—	117

These first results clearly demonstrate that even low levels of Ag in suspended or solid form can be speciated by Ag K-edge XANES and EXAFS spectroscopy. We plan further studies to investigate the fate of silver nanoparticles of different sizes and with different surface functionalization during wastewater treatment in order to provide a robust basis for the assessment of their transmission into the aquatic environment. Ag K-edge XAS will represent the perfect tool to rationalize macroscopic observations on the basis of distinct chemical species.