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:** In situ time-resolved SAXS study of the nucleation growth and crystallisation of Al, Si and Fe (oxy)hydroxide nanoparticles	**Experiment number:** **ME-843**
Beamline: BM26	**Date of experiment:** from: 6/7/05 to: 11/7/05	**Date of report:** 10/08/05 *Received at ESRF:*
Shifts: 15	**Local contact(s):** Florian Maneau	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Al (oxy)hydroxide e.g. boehmite (-AlOOH), silica (SiO2) and ferric iron nanoparticles are commonly found in mine drainage areas, acid rain effected forest environments and hot spring deposits. They form by the neutralisation of acidic or basic surface and groundwater containing dissolved Al, Si or Fe species. Al species (e.g. Al(H2O)63+) in groundwater are known to be toxic to tree roots and colloidal Al (oxy)hydroxide precipitates in surface water can cause significant environmental damage to fish populations and aquatic vegetation. Al, Si and Fe (oxyhydr)oxide nanoparticles can also sorb toxic contaminants (e.g. As5+, Zn) from solution during and after formation causing a significant reduction in aqueous-phase trace element concentrations. Therefore, to understand the effects of these phases in the natural environment it is important to understand their formation mechanisms and kinetics and the means by which they sequester contaminant ions.

The hydrolysis of aluminium, silica and iron in solution was studied using a stopped-flow reaction cell and a newly developed flow-through reaction cell. The formation of poorly order iron oxyhydroxide nanoparticles were characterised as a function of temperature (Figure 1). Experiments were performed at 4ºC and 10ºC, to complete a full temperature series from 4-50ºC (other temperature experiments performed during previous DUBBLE beamtime). Figure 1a shows time resolved SAXS data for the formation of poorly ordered ferric oxyhydroxide nanoparticles at 10ºC. The data is of a high quality, accurate particle size (fig1b) and shape information can be obtained. The data will also allow a detailed examination of the formation energetics (i.e. activation energies of nucleation and growth) of these phases.

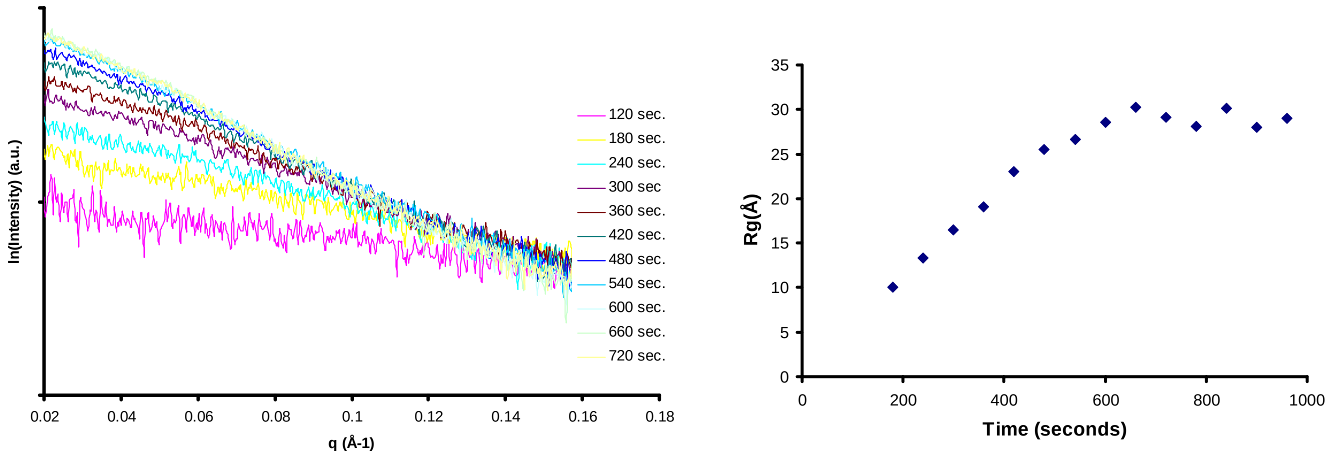

Figure 1a. Time-resolved SAXS data for the formation of ferric oxyhydroxide nanoparticles at pH 3 and 10^{o}C and (b) the Rg of the nanoparticles as a function of time..

Al oxyhydroxide formation was characterised using an automated base titration system which used a flow through reaction cell to monitor the formation of nanoparticles as the pH of a 0.1 M $Al(NO_3)_3$ was raised by the addition of 0.1 M NaOH. Figure 2 shows the invariant and radius as a function of pH determined form the SAXS data. The formation of scattering particles/ solution complexes begins at pH≈4.5 and are stable until pH 5.5. The invariant and particle size then increase rapidly as precipitation occurs. The colloid then remains stable until pH 9.5 where the particle size again increases probably due to recrystallisation at high pH

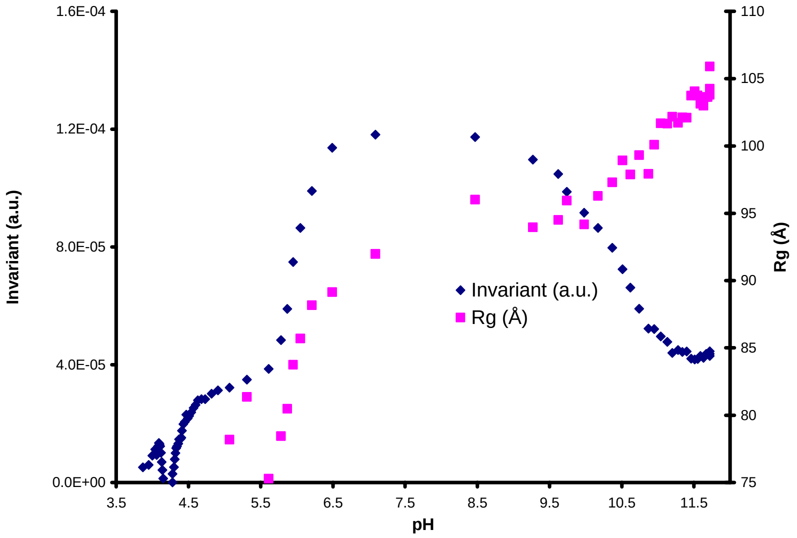

Figure 2. Invariant and radius of gyration as of function of pH for particles/solution species formed during the hydrolysis of a 0.1M $Al(NO_3)_3$ solution

The nucleation and growth of amorphous silica particles was also studied as a function of pH to model the formation of silica from silica enriched (0.1M Si) natural waters associated with hot spring deposition of silica in volcanic environments. Analysis of this data is currently on going.