	Experiment title:	**Experiment number**:
	In situ, time resolved Small Angle X-ray Scattering (SAXS) of the nucleation kinetics of iron sulphides and oxihydroxides	SC-789
Beamline: ID2	**Date of experiment**: from: May 03 2001 to: May 06 2001	**Date of report**: 14/08/01
Shifts: 9	**Local contact(s)**: Dr. Pierre Panine	*Received at ESRF:*

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Report:

Introduction

Iron sulphide and oxyhydroxide phases are the principal iron bearing minerals in all geologic environments. In laboratory experiments, poorly ordered phases (amorphous FeS and ferrihydrite) form instantaneously when a ferrous / ferric iron solution is mixed with a sulphide / hydroxide solution. In natural environments, Fe-S and Fe-OH phases occur as ultra-fine particles (2-200 nm) suspended in anoxic and oxic waters or as coatings on mineral grains. Their high specific areas and very reactive surfaces enable them to control the mobility of toxic trace elements (e.g., As, Cd, Cr). However, the factors governing their nucleation and growth are still equivocal despite their vital importance in a large variety of natural and industrial/environmental processes. For example, Fe-S phases are believed to be important in controlling the redox conditions favorable for the formation of early pre-biotic life on Earth and in scavenging toxic metals from acid mine drainage systems, while iron oxyhydroxides are common colloidal phases that control the mobility of hazardous radioactive contaminants in near-earth surface environments. Consequently, the development of effective remediation strategies is dependent on the basic understanding of the kinetics and mineral formation mechanisms in the Fe-S and Fe-OH systems.

The first steps in the formation of these phases are equivocal because the formation reactions are extremely fast and are strongly pH, redox and temperature dependent. We show here that the use of small angle X-ray scattering (SAXS) in conjunction with a stopped-flow cell is ideal to characterise these first stages (<100ms to ≈60 s) of the nucleation and growth of colloidal ferrous sulphide and hydrated ferric oxide phases. The goal was to provide information on size distribution, particle morphology, and possibly fractal dimension during precipitation from solution.

ID2 is a High-Brilliance beamline situated on an undulator source in a high-ß section of the storage ring at the ESRF. Only the central radiation cone of the undulator is used delivering a high flux of monochromatic photons ($8x10^{12}$ph/s) with low divergence through a sample cross-section of typically 100 µm x 300 µm (v x h). The optics are optimised for experiments using a fixed wavelength around 1Å (12keV), but wavelengths between 0.73Å and 1.55Å are accessible, making this station ideal for fast dynamic studies. The station is

only let down by the comparatively slow read out time of its primary detector system. The Thomson X-ray Intensifier (TH 49-427) lens coupled to the ESRF developed FReLoN CCD camera has developed into an excellent detector. It has an active area of 230mm (1024x1024 pixels) with a nominal dynamic range of 14 bit, yet data collected in 10msec, still requires 0.1sec to read out to memory.

Experimental Methods

All solutions (Fe^{2+}, Fe^{3+}, $H_2S_{(aq)}$, KOH) were prepared in the fume hood of the chemistry laboratories of the ESRF. The ferrous iron and sulphide solutions were prepared in special, glass-reactor systems (provided by the PI's) that were kept oxygen-free by purging with ultra-high-purity nitrogen. For the ferrous iron (Fe^{2+}) solution, Mohr's salt [$Fe(NH_4)_2(SO_4)_2$] was used, while for the sulphide solution O_2-free doubly distilled water was saturated at 1 bar with H_2S gas. The Fe^{3+} and KOH solutions were prepared from ferric nitrate [$Fe(NO_3)_3$] and KOH pellets respectively. Prior to each experiment, the solutions were degassed to remove the possibility of bubble formation during mixing, and aliquots of the stock solutions were transferred to syringes sealed with 3-way valves that were subsequently connected to the Bio-logic stopped-flow apparatus. The Bio-logic stopped flow cell system has a quartz sample capillary, 3 reservoir syringes and 2 mixers. The dead volume is ~ 10 µl and the dead time of 10 milliseconds can be achieved (see http://www.biologic.fr).

During each experiment, calibrated aliquots of each solution were injected at constant time intervals into the reaction cell via a mixing chamber and the changes in SAXS patterns were observed over time. By varying the mixing ratios, and therefore the concentration of iron and the pH of the solutions the products and the reaction rates were varied. Time-resolved SAXS data was collected on time scales of 20 to 500 milliseconds per scan with the total length of an experiment varying between 2 seconds to 15 minutes.

Preliminary Results.

We have conducted experiments at various time frames:

(a) experiment total time = 2 sec, corresponding to 20 frames a 20 milliseconds with 100 millisecond dead time;
(b) experiment total time = 20 sec, corresponding to 20 frames a 500 milliseconds with 100 milliseconds deadtime;
(c) experiment total time = 60 sec, corresponding to 60 frames a 500 millisecond and 100 millisecond deadtime and
(d) experiment total time = 15 min, corresponding to 30 frames a 500 milliseconds with 29.500 milliseconds deadtime.

In the 2 second experiments the nucleation of FeOOH particles is occurring within the first scan - i.e., first 120 milliseconds and the growth of these particles can be followed for the whole length of the experiment (Fig. 1). In the longer time scale experiments the nucleation, growth, and possible later dissolution can be followed (Fig. 2; total time =60 sec). Once the Rg and Io are calculated for the various mixing ratios (Fe^{2+}/Fe^{3+} to H_2S/KOH, i.e., differing pH and Fe^{2+} /Fe^{3+} concentrations) the data can be analysed using an Avrami type kinetic model to determine reaction rates and growth mechanisms. Figure 3 and 4 show this for both, the FeOOH and the FeS systems. These initial runs have clearly shown that fast light scattering experiments using the stopped-flow system and can be carried out successfully and that kinetics of nucleation and growth of colloidal particles in these two systems can be followed at very fast reaction times. However, further experiments are needed at a variety of camera lengths and with a various mixing ratios to fully evaluate the kinetics of these systems. Such information will help to fully determine the reaction kinetics and provide a basis for the sound description of the nucleation, growth and aggregation processes occurring in both systems. In addition, the morphological changes (size, shape) of the precipitated colloidal particles over time, and at varying pH and temperature can be calculated.

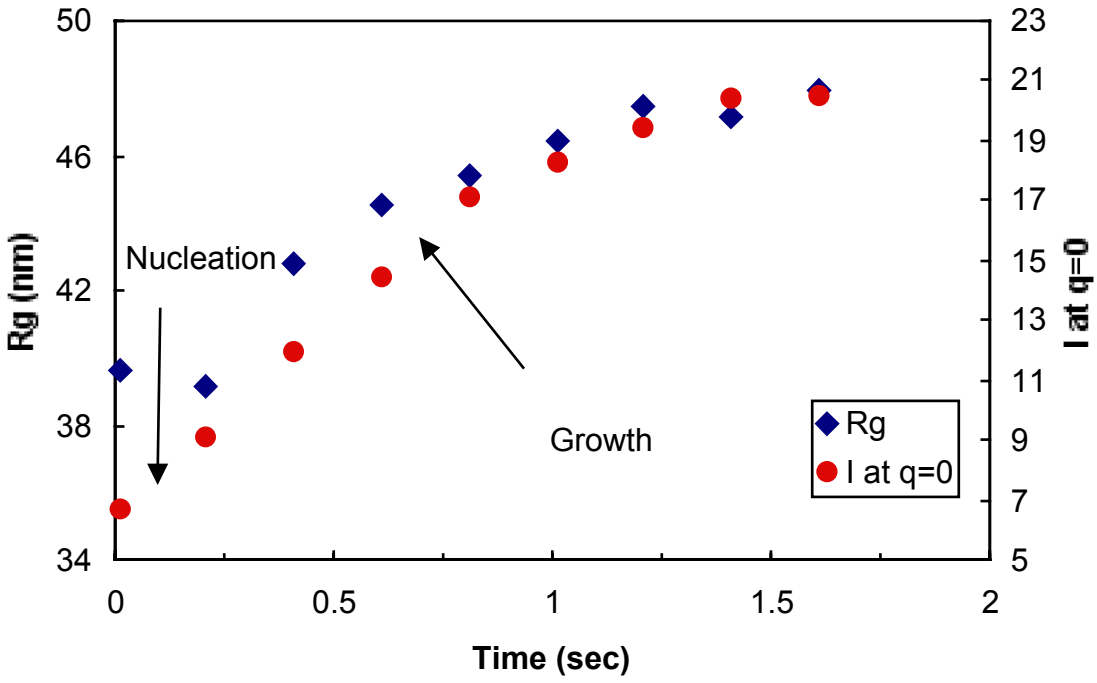

Figure 1. Radius of gyration and I (at q=0) vs. Time for FeOOH particles in an experiment at 6.5 meter camera length and 2 second duration, with 20 frames collected for 20 milliseconds each with 100 milliseconds deadtime between scans.

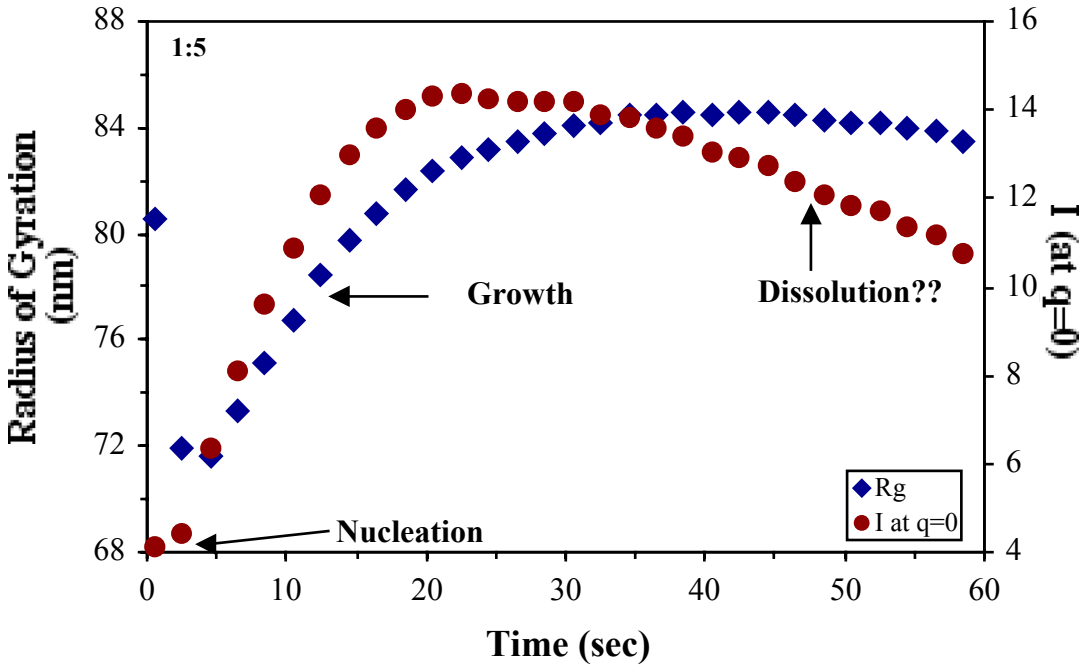

Figure 2. Radius of gyration and I (at q=0) vs. time for FeS particles in an experiment at 6.5 meter camera length and 60 second duration, with 60 frames collected for 500 milliseconds each with 500 milliseconds deadtime between scans.

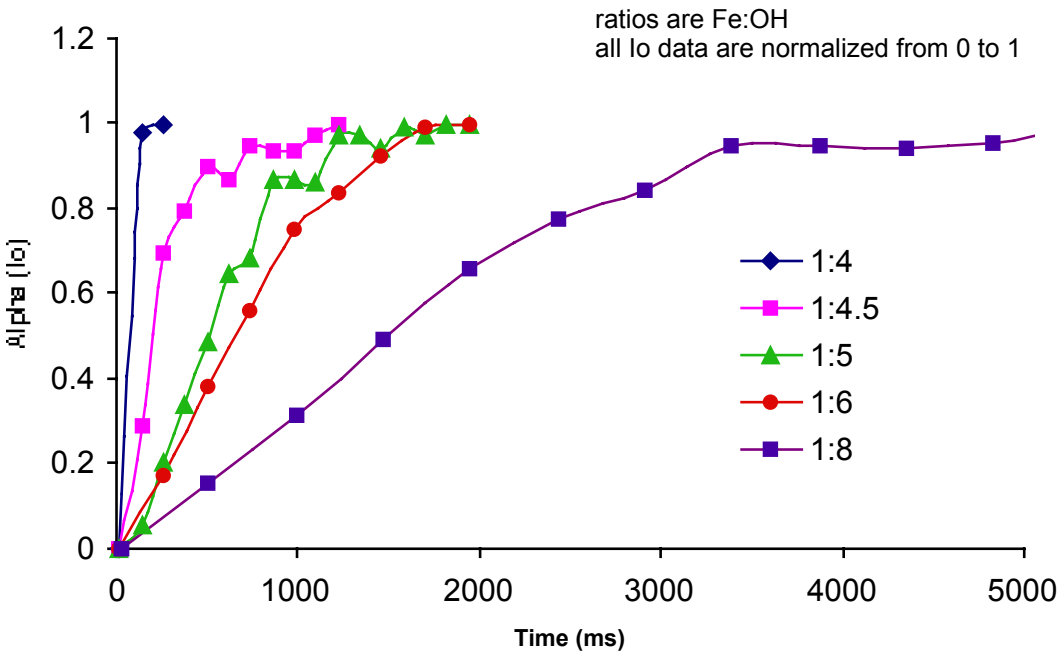

Figure 3. Alpha (Io) vs. Time for the various mixing rations in the FeOOH system at 6.5 meter camera length.

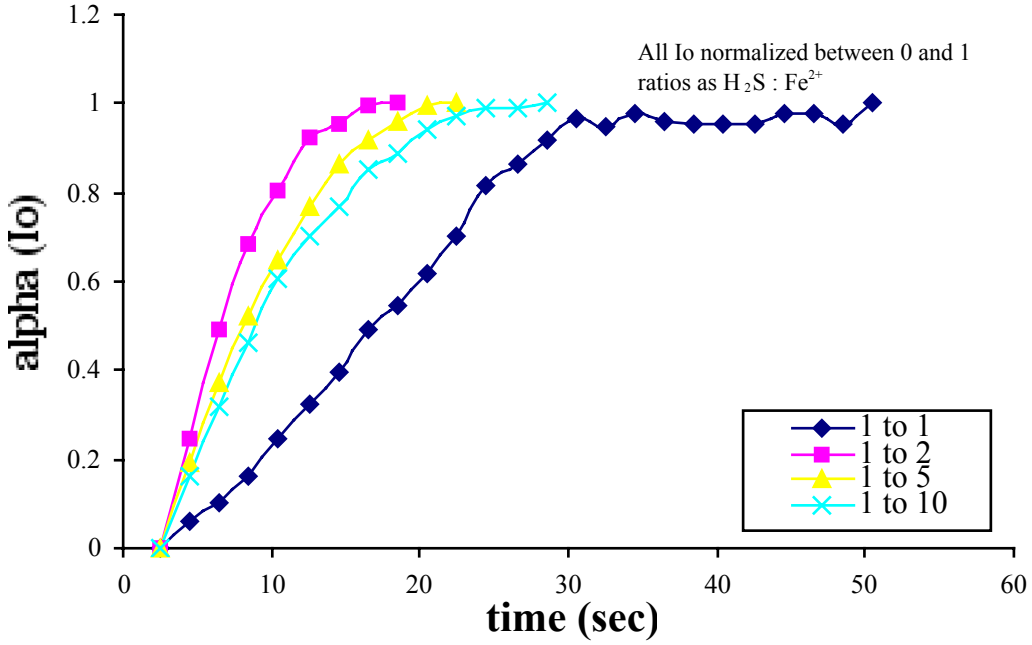

Figure 4. Alpha (Io) vs. Time for the various mixing rations in the FeS system at 6.5 meter camera length