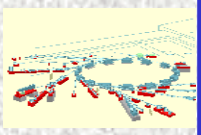
In situ, Time Resolved Small Angle Solution X-ray Scattering:

Nucleation and growth of iron based colloids



Liane G. Benning[1]

S. Shaw[2], N. Terrill[3], P. Panine

[1] School of Earth Sciences, University of Leeds, UK, (liane@earth.leeds.ac.uk)

[2] Department of Geology, Oxford University, UK; [3] Daresbury Laboratory, Warrington, UK

[4]European Synchrotron Radiation Source, Grenoble, France

Introduction:

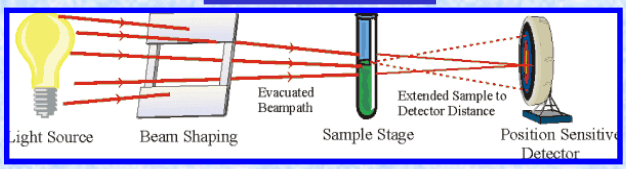
The migration of toxic contaminants (cations, anions, and organics) in many near-earth surface environments is controlled by their interaction with poorly ordered iron sulphide (mackinawite) and iron oxide (ferrihydrite) phases. However, the mechanisms and kinetics of the nucleation and growth of colloidal Fe-S and Fe-OH particles from aqueous solution are poorly known.

Goals and means:

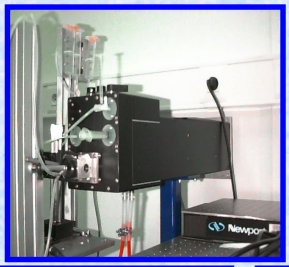
Here we present results from synchrotron-based, time-resolved Small Angle X-ray Scattering (SAXS) experiments that followed the nuc leation and growth kinetcis of Fe-based colloids from aqueous solution.

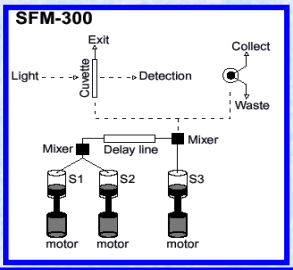
When SR is elastically scattered by a sample the resulting pattern can provide information about the **kinetic rates, the growth mechanism** and the **morphology** of nanoparticles.

Experimental methods:



- station ID2 at the European Synchrotron Radiation Facility
- undulator source (flux = 8×10^{12} ph/s); low divergence;
- optics optimized for a fixed wavelength of ~ 1 Å (12 keV)





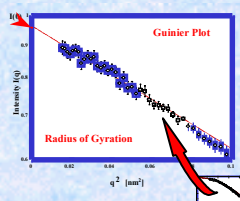
Stopped flow system

- **fast and accurate mixing,**
- **< 10 ms deadtime**
- **T - 25 - 80ºC**
- **oxic or anoxic**

Experimental conditions

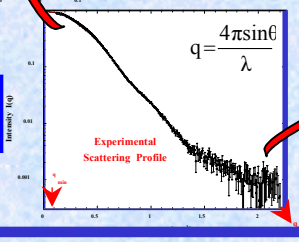
- **Fe^{2+}/ Fe^{3+}: H_2S/ KOH; ratios → 1:1 to 1:10**
- **20 → 500 milliseconds / scan**
- **2 sec → 60 sec total time / run**

Results:



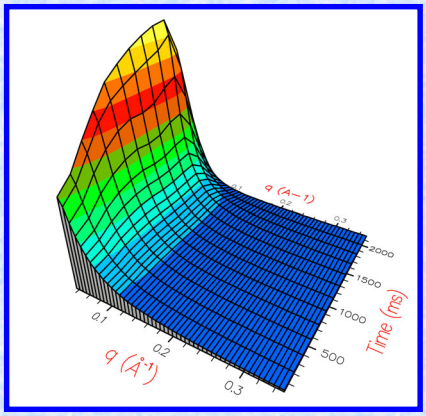
Rg = slope
= shape function independent radius

I (at q=0) = intercept
= # particles / volume of solution



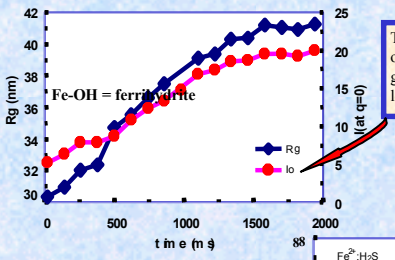
- **Low *q* = radius**
- **High *q* = shape**

a priori Shape Reconstruction



On the left, a 3-dimensional plot of the results from an experiment where a Fe^{3+} and a KOH solution were mixed at a ratio of 1:5 and where SAXS patterns were collected every 20 milliseconds is shown.
At the 2 second time scale it can be seen that the relative intensity of the scattering increases and this was used to derive the changes in radius of gyration and Io.

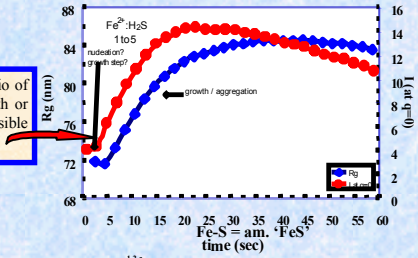
(x-axis = scattering vector q in $Å^{-1}$, y-axis= relative intensity and z-axis= is time in milliseconds)

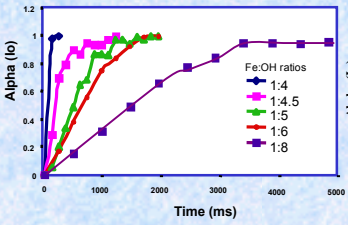


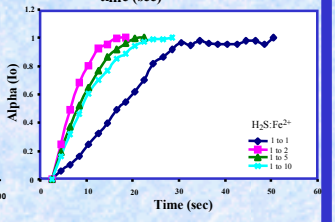
The nucleation of FeOOH particles occurs very fast (<120msec) while the growth can be followed for the whole length of the experiment.

The small variation in Rg values indicates that the different contrasts yield very similar size distributions.

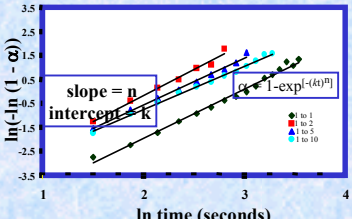
In the Fe-S system at a mixing ratio of 1: 5 the nucleation (<2sec), growth or aggregation (<25sec) and the possible re-dissolution is shown.







Kinetic rates and mechanisms were derived from experiments (and from the calculated Rg and Io) at various mixing ratios via an Avrami type equation with α normalized to 1.



Summary

The *in situ* nucleation and growth of colloidal particles in the Fe-S and Fe-OH system has been determined using solution SAXS. The data has been used to resolve **growth kinetics**, **particle size** and **morphology** of structures forming at the millisecond to second timescales.

In environments where the growth of such colloids affect the behaviour of toxic trace elements (e.g., acid mine drainage, waste water treatment), this kinetic data can be used in planning the nature of the remediation procedures.

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