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# The Nucleation of Particulate FeS Observed with Small- and Wide Angle X-ray Scattering

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## Introduction

Amorphous FeS and mackinawite are the principal iron minerals nucleating at low temperatures when aqueous ferrous iron and dissolved sulphide solutions are mixed. Their formation for example in marine sediments controls a major part of the global iron and sulphur cycles. The nucleation of these phases is pH, redox and temperature dependent and occurs at very fast times scales (hundreds of millisecond; Rickard, 1989). Therefore, such reactions are difficult to monitor. Here we present preliminary results from an experimental study that made use of a synchrotron-based simultaneous small- and wide-angle X-ray scattering (SAXS/WAXS) method that can provide a direct means of probing *in situ* and in real time the structure of different components in a matrix of contrasting electron density. This method is ideal for determining the long range ordering and formation of amorphous structures and their subsequent transformation to crystalline products. The information inherent in the SAXS patterns can be correlated with variations in particle size, and in the ideal case, they enable the determination of the particle density, shape, and size distributions. In addition, the potential to record simultaneous SAXS/WAXS patterns as a function of time and temperature provides a means of assessing reaction mechanisms and kinetic rates. This method was used to determine the primary steps in the formation of amorphous iron monosulphide compounds and their subsequent crystallisation to mackinawite in aqueous solutions at 25°C.

## Methods

Experiments were carried out on station 8.2 of the Daresbury Laboratory. A remotely controlled stopped-flow cell system was used and ferrous and sulphide solutions were mixed *in situ* in the beam and reaction progress was monitored over time. The stopped-flow cell was fitted with two solution containers into which the solutions were injected under nitrogen via three-way valves fitted with syringes. Solutions of various concentrations were prepared off-line and each experiment commenced by mixing various ratios of the two solutions in the cell via two remotely controlled simultaneously operating solenoid valves. Special care was taken to avoid oxidation and the preparation methods described by Benning et al. (2000) were followed. Both the SAXS and WAXS data were collected at 1 millisecond to 1-minute time scans in transmission mode. Each experiment was repeatedly cycled for up to 200 times to improve statistics. The data acquisition and reduction was done with Daresbury software (VME with synchronized time framing, and XOTOKO and XFIT; de Moor et al., 1997 and Shaw et al., 1999).

## Results

Preliminary results show that in the FeS system at low pH and low concentrations, first nucleation occurs after about 30 milliseconds and the main precipitation is over within about 20 milliseconds. However, in some cases, part of the precipitate re-dissolve in the next 100 milliseconds before equilibrating as the final product, process presumably attributable to localised changes in pH. In general, the nucleation reaction times are fast (30-100 milliseconds) but at high iron and sulphide concentrations the small angle pattern shows continuous growth of particles for up to 30 minutes.

## Conclusions

Small and wide angle X-ray scattering experiments can be used to monitor nucleation reactions at times scales of several 10 to 100 milliseconds. It could be shown that the fast nucleation of iron monosulphide phases can be monitored. Further work will concentrate on determining kinetic reaction rates for these reactions.

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