

Experiment Report Form



	Experiment title: Characterisation of structural disorder in goethite with various amount of heavy metals	Experiment number: ES-609
Beamline: ID22	Date of experiment: from: 16/02/2018 to: 20/02/2018	Date of report: 25/02/2018
Shifts: 12	Local contact(s): Mashikoane Wilson Mogodi	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Monica Dapiaggi*, Università degli Studi di Milano, Milano, Italia. Dr. Giorgia Confalonieri*, Università degli Studi di Torino, Torino, Italia. Dr. Nicola Rotiroti, Università degli Studi di Milano, Milano, Italia		

Report:

- Introduction

This experiment is a first step of a wider project concerning Acid Mine Drainage (AMD) process, which has a very dangerous effect on the environment. During AMD, various disordered ferric hydroxides and oxy-hydroxides are formed, leading to the potential release of heavy metals in the environment. This very first part of the project aims to the structural characterization of the disorder in natural and synthetic goethite (which is the simplest of these materials), as they are, and doped with Pb. Rietveld method and Pair Distribution Function will be applied in order to characterized these materials on the average and local structure.

- Materials

Different samples were prepared starting from a synthetic commercially available goethite (Sigma-Aldrich), which was used as reference sample. Pure goethite was doped with different lead amounts by absorption of cations from a solution of lead nitrate with different concentrations (1, 5, 10, 50 mM). Goethite was left in contact with the Pb-containing solution for 24h, and then filtered. Two sample-sets were prepared taking into account two rinsing treatments: i) samples rinsed once in water ii) samples rinsed twice in water. The solid residual was then heated at 200°C in order to facilitate the incorporation of lead into the structure. In addition also two natural samples were investigated.

Samples	Pb concentration	Treatment
Goethite Reference		
Goethite1	1, 5, 10, 50 mM	Single rinsing
Goethite2	1, 5, 10, 50 mM	Double rinsing
Natural Goethite 1		
Natural Goethite 2		

Table 1: investigated samples

- Data collection

Total scattering data was collected by multyanalizer detector using a short wavelength (0.354379 Å) in order to achieve high resolution on the reciprocal and direct space. Each data collection lasted 3 hour to obtain high counting statistics at high Q, indispensable to obtain then suitable Pair Distribution Functions. Some selected samples were collected also at 80 K for a better signal, with less thermal diffused scattering.

- Results

Samples synthetically prepared were compared between them and with the reference sample. As demonstrated by figure 1, samples doped with different amount of lead and treated with different leaching treatment (Goethite 1 and 2) show differences in peak position. This demonstrates a different amount of incorporated lead.

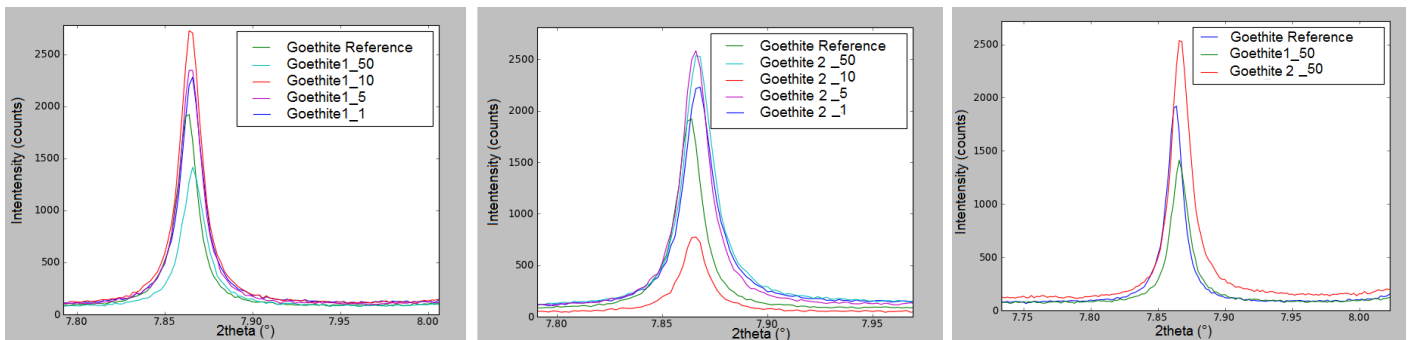


Figure 1: comparison of diffraction patterns between samples prepared with Pb and the reference.

In table 2 and 3 cell parameters of two samples treated by different rinsing treatment are reported comparing also values of the reference sample. Doped samples present smaller volume values due to the incorporation of Pb. The same can be seen, for the same sample set (goethite1 or goethite2) as a function of starting lead content.

Sample	Cell Volume (Å ³)
Goethite Reference	138.72(2)
Goethite 1_50	138.60(2)
Goethite 2_50	138.61(2)

Table 2: cell volumes for some samples treated with different rinsing treatment

Table 3: cell parameters for some samples treated with different rinsing treatment

Sample	a (Å)	b (Å)	c (Å)
Goethite Reference	4.60586(7)	9.96281(5)	3.02306(2)
Goethite 1_50	4.60434(7)	9.96274(4)	3.02160(4)
Goethite 2_50	4.60446(8)	9.96416(1)	3.02121(4)

Furthermore, by looking figure 1, the different rinsing treatments for sure influence the adsorbed lead released. Indeed, despite similar cell parameters, samples rinsed just once (goethite1), presents broader peaks. This could be related to a possible local disorder. As demonstrated in figure 2, doped samples present some differences at the local scale in comparison to the reference sample, in particular some PDF peaks, especially those related to Fe-Fe distances, tend to have the same position as those of the reference sample, while other (Fe-Fe as well as Fe-O distances) have a different position and a different shape, with respect to each other and to the reference sample. Moreover the two rinsing treatments seem to originate structural differences also at the medium scale (see figure 2, right hand side). Deeper studies will be performed in order to describe and characterized these differences.

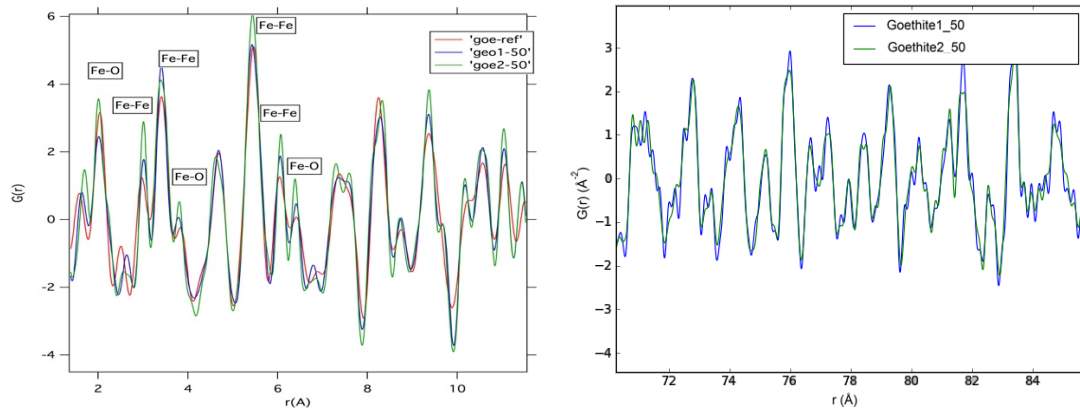


Figure 2: PDFs of two samples treated with different rinsing treatments are presented at the local (left side) and at medium scale (right side). In the left panel also theoretical Partial PDFs are reported.

Unfortunately, the experiment was performed from the 16th to the 20th of February, so the results presented here are only very preliminary.