![ESRF] ESRF	**Experiment title:** Understand and predict Fe(III)-promoted oxidation of abandoned sulfidic mine tailings	**Experiment number**: EV-439
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Report:

Context and objectives:

Tailing covering is foreseen as (part of) a solution for reclamation of acid leaching mine tailings of Folldal (central Norway) and Doyon (Quebec, Canada), as this approach has proven efficient in several sites (Demers and Pabst, 2020). However, column experiments suggest that oxygen limitation is not sufficient to decrease significantly the rates of sulfide oxydation in these weathered tailings (Dublet et al., 2021). It is hypothesised that Fe(III) oxydes from the weathered mine tailings are mobilized at low pH and oxydize sulfide minerals (mainly pyrite). A geochemical model was attempted to explain oxidation reaction occurring with limited oxygen, using XRD-detected iron(III) phases as a starting point (2 wt% jarosite in the HS tailing tested in columns, see Table 1). The model underestimated sulfide oxydation. Because XRD is not sensitive to poorly cristalline phases, is suspected that poorly cristalline Fe(III) oxyhydroxydes were overlooked. One first objective was thus to determine the presence and proportion of Fe in iron oxyhydroxydes using an approach specific to Fe and sensitive to poorly crystalline phases. Under the pH-Eh conditions of the experiment, other Fe(III) phases than jarosite would be relevant, like schwertmannite and ferrihydrite. Therefore, a second objective was to identify the nature of Fe-phases using Fe K-edge EXAFS.

Analyses done:

We analysed Fe K-edge EXAFS in three mine tailings representing contrasted materials found at the Folldal mine, as well as high-sulfide tailings after 180 days of column leaching with or without a cover with capillary barrier effect (CCBE) and the solid phase of simple batch reaction tests under ambient or suboxic conditions after 21 and 100 days. In addition, we analyzed reference compounds, i.e. pyrite, chalcopyrite, ferrihydrite, schwertmannite, and Na-jarosite. The initial idea, as described in the proposal, was to also use reference EXAFS spectra from a wide variety of model compounds in order to analyse our EXAFS data by LC-LSF. Due to technical problems during the two last shifts (failing of the cryostat pump) the Canadian tailings could not be analyzed.

Samples were crushed with a planetary mortar and then by hand with a mortar and pestle, and the mixed with boron nitride. We recorded long-range EXAFS at 20 K in order to be able to distinguish different families of iron oxides (Thomas et al., 2018). Because the concentration of Fe in the tailings was generally very high (0.1-4 wt%), EXAFS were registered in transmission mode. Unfortunately, normalisation to the incident beam signal was not sufficient to compensate the beam fluctuations after k=10.2, especially for the most diluted samples. This led to oscillations that were not yielded by absorption by the sample itself and that added to the EXAFS signal (Figure 1). Crushing and homogenizing longer time did not improve the quality of the data sufficiently. We also had similar problems with reference samples of pure Fe(III) hydroxides, e.g. ferrihydrite and schwertmannite (Figure 1). Fluorescence detection was also attempted on a few samples

diluted in more boron nitride, but self-absorption was too high due to the speciation of Fe (in grains of pyrite, for example). It was thus decided to use only the EXAFS data at k=10.2 and perform LC-LSF on those shorter EXAFS data.
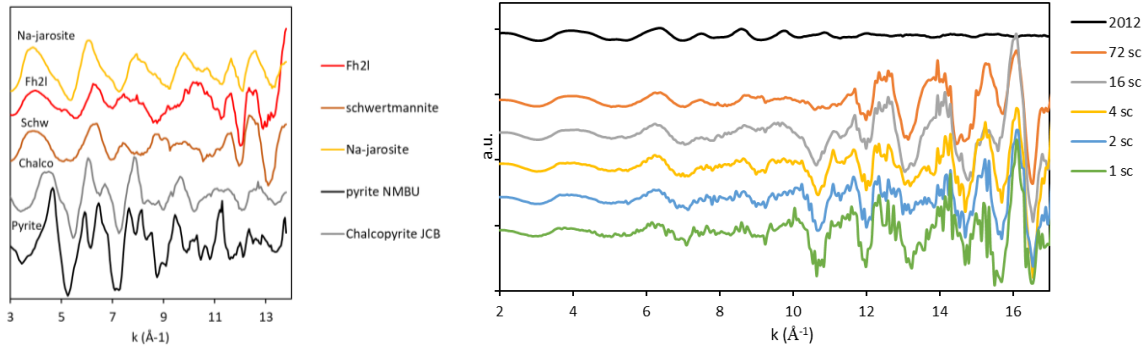

Figure 1: Left: Fe K-edge EXAFS spectra obtained for reference compounds. Right: illustration of non-EXAFS oscillations at k>10.2, with the example of the schwertmannite reference. " x sc" = number of scans averaged. A reference of schwertmannite recorded at another beamline (SAMBA, SOLEIL) in 2012 by Morin et al is shown ("2012", in black) for comparison.

Results

Here are presented EXAFS data at k=10.2 for the three "parent" tailings and the HS tailings after 180 days of column tests.
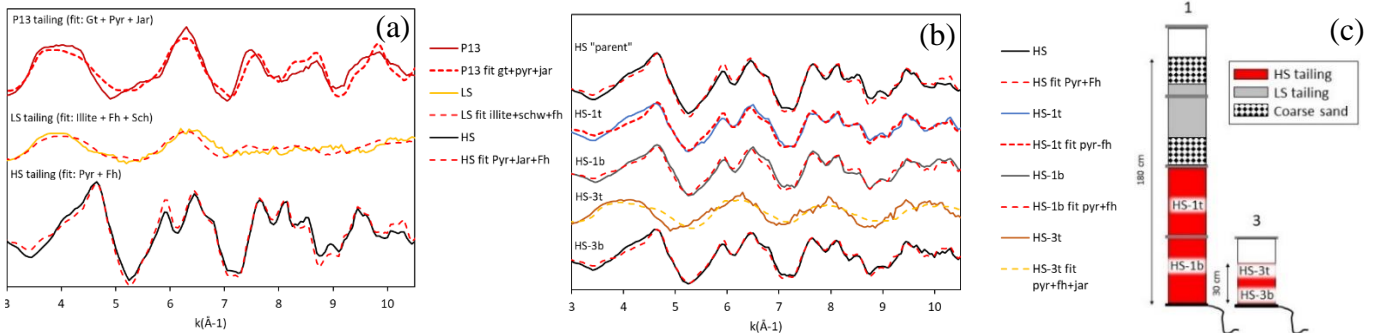

Figure 2: Fe K-edge EXAFS of the three mine tailings from the Folldal site (a) and from the HS tailings after 180 days of column leaching (b). HS tailings and LS tailings are "parent" tailings used for in column tests (Dublet et al., 2021; Figure 2). P13 is an additional "parent" tailing representative of another material widely found at Folldal, also used in batch leaching tests for which the solid phase was analysed by Fe K-edge EXAFS during this beamtime (results not shown). Dashed lines show the LC-LSF fits with reference compounds (Table 1). (c) Localisation of the samples analysed in the column tests (left) and corresponding Fe K-edge EXAFS spectra (right). Dashed lines show the LC-LSF fits with reference compounds (Table 1).

Conclusions:

Table 1: Comparison of Fe phases detected with XRD (yellow), the normalized distribution of Fe among these phases if they represented the whole Fe pool (blue) and the Fe distribution among mineral species as determined by LC-LSF of Fe K-edge EXAFS (pink).

	XRD results (wt%)				Fe distribution (%) hypothetical based on XRD			Fe distribution based on Fe K-edge EXAFS				
	pyrite	jarosite	hematite	goethite	pyrite	jarosite	Gt/Hem/Fh	pyrite	jarosite	Gt/Fh/Hem	Schwertmannite	Phyllosilicates
	FeS2	$(Fe(SO_4)_2(OH)_6)$	Fe2O3	FeOOH	FeS2	$(Fe(SO_4)_2(OH)_6)$						
HS tailings	9	2			92	8	0	69	14	17		
LS tailings		1			0	100	0			20	18	63
P13	8	3	6	29	14	1	84	0.3	13	87		
HS-1t	18	4			94	6	0	79		21		
HS-1b	24	4			95	5	0	62		38		
HS-3t	7	64% sulfates*			ND	ND	ND	14	51	36		
HS-3b	17	4			93	7	0	65		35		

*64% of sulfates (mainly magnesiocopiapite, $MgFe^{3+}_4(SO_4)_6(OH)_2$) were identified with XRD, and jarosite seemed to account for these compounds.

1) These results confirm the hypothesis formulated in Dublet et al 2021 about HS tailings, i.e. that these tailings contain significant amounts of poorly crystalline Fe(III) oxyhydroxides that were not detected by XRD.

2) The reduced chi^2 of the LC-LSF of Fe K-edge EXAFS spectrum of the HS tailing is 15% better if chalcopyrite is added. No chalcopyrite was identified by XRD, but some was observed by SEM. If chalcopyrite is added to all of the LC-LSF fits, it represents 13-15% of total Fe in the column tailings HS-1t, HS-1b and HS-3b, while it does not occur in HS-3t, which is the most exposed to oxidation without cover. This result comforts the hypothesis that chalcopyrite oxidation is responsible for the high Cu concentrations leached out of the uncapped column tests.

3) No Fe-bearing phase was clearly identified by XRD in LS tailings. Fe K-edge EXAFS results suggest that most of Fe is distributed within Fe(III) phyllosilicates and oxyhydroxydes (schwertmannite and ferrihydrite compounds were best for the LC-LSF fit). This result supports the hypothesis proposed in Dublet et al 2021 concerning a potential transport of Fe(III)-oxydes from the LS-tailings used as a cover material, to the HS-tailings under. Sources of Fe(III) to be considered in the geochemical model should thus be both Fe(III) from HS tailings itself, and Fe(III) from the overlying LS tailings.

4) Fe speciation in P13 found with Fe K-edge EXAFS seems in agreement with the mineral distribution determined by XRD. Indeed, most of Fe is hosted by Fe(III) hydroxides (a well crystalline goethite was used in the fit presented) and jarosite. The proportion of Fe in jarosite, however, may be higher that that suggested by XRD.