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DECTRIS

ARINA with NOVENA

Fast 4D STEM



DECTRIS NOVENA and CoM analysis of a magnetic sample.

Sample courtesy: Dr. Christian Liebscher, Max-Planck-Institut für Eisenforschung GmbH.
Experiment courtesy: Dr. Mingjun Wu and Dr. Philipp Hein, Friedrich-Alexander-Universität, Erlangen-Nürnberg.

Meeting-report

Arsenic Fixation by Aged Ferrihydrite Nanoparticles

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Ferrihydrites (Fh) are metastable iron oxyhydroxides, common in the soils [1]. This nanoparticulate solid phase plays an important role in the transport and fixation of pollutants, among them the arsenic [2–5]. The heavy metals removal capacity of Fh may be affected by isomorphic substitution and in the mineral the most common substituents are Al and Si [6, 7]. Therefore, understanding the role of Al in Fe oxyhydroxides for As removal and fixation is crucial for the comprehension of As fate in the soils and for the development of remediation technologies.

An Oxisol used as a chemical barrier in tailings dams of sulfide concentrate, during over 10 years, have shown good As uptake [8, 9]. The soils were found to be rich in Al and Fe. In fact, the Al substitution in Fh has been found to increase up to 30% the As removal [10]. In the Oxisol, more than 60% As immobilized in Al-Fe-mesocrystals, suggesting an entrapment of the metalloid in the oxyhydroxides nanostructures.

In that context, this work aims to investigate the role of Al in Fh structure on the mesocrystals formation and As fixation, by studying the combined effects of aging Al-for-Fe substituted Fh and exposure to environments containing As, in phase transformations, as well as in the remobilization of As.

The 2-line ferrihydrites (Fh) were prepared following the method of Schwertmann and Cornell [11]. The method was modified to include aluminum in molar ratios of Al / (Fe + Al) 0, 0.05, 0.10, 0.15, 0.20 and 0.25. Ferrihydrites suspensions, containing or not As, were put in covered polyethylene bottles and submitted to 30 or 70 °C in a thermostatic bath. The supernatant's chemical composition was analyzed by ICP-OES (Perkin Palmer 7300). The solid samples were dissolved in 8% aqua regia to analyses As, Al and Fe. Powdered samples were submitted to X-ray diffraction (XRD) by using a Philips (Panalytical PW1710) X-ray diffractometer, with Cu (K α) radiation, tube voltage of 35kV and current of 50 mA. The diffraction patterns were compared to the reference powder diffraction file (PDF), from Inorganic Crystal Structure Database- FIZ Karlsruhe (ICSD).

The XRD of samples aged during 580 days at 30 °C indicate that the Al presence retards the oxyhydroxide phase transformation as well as prevent goethite formation (Fig. 1).

The Al presence was also shown, by TEM, to favor the formation of mesocrystals, likely grown by oriented aggregation. The Fig. 2 compares the nanocrystals formed by the aging of FhAl-0% and FhAl-10%, highlighting the oriented aggregate in the last.

During the aging experiments in the presence of As, the metalloid concentration dropped down from [As] = 100 mg kg⁻¹ to 0.05 mg kg⁻¹ (Fig. 3) and stabilized below this concentration during the aging time. The results indicate that the As was likely incorporated into the new iron oxyhydroxide phases formed by the aging. Such incorporation may be favored by the mesocrystals formation in the Al substituted Fh.

To corroborate the hypothesis of As incorporation in the mesocrystals the samples were analyzed by atomic resolution HAADF-STEM imaging, using an aberration corrected FEI Titan Themis microscope. The HAADF-STEM images of the mesocrystals show atoms with a higher Z-contrast in the Fe atomic column, which suggests those sites may be occupied by As (Fig. 4). EDS analysis and mapping shows As distributed across the mesocrystals. Atomic resolution EDS mapping was unsuccessful though, as the As content is relatively low to integrate enough signal mapping at high resolution. These results indicate that Al delays Fh phase transformation and favors mesocrystal formation. The data supports our hypothesis that As is entrapped into the mesocrystal as they form by oriented aggregation. As FH transforms to more stable phase hematite, it remains into the lattice. This mechanism successfully explains As fixation in soils [12].

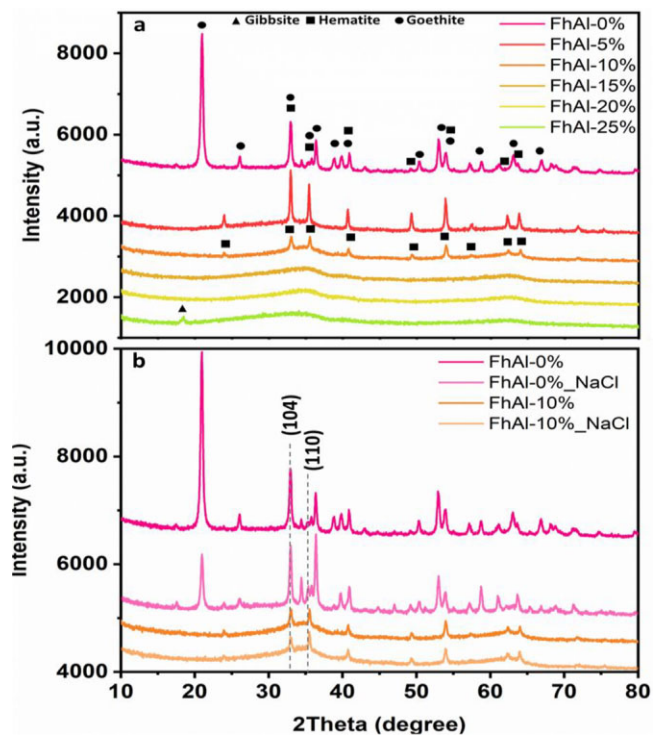


Fig. 1. XRD of Fh aged during 580 days at 30 °C of samples FhAl.

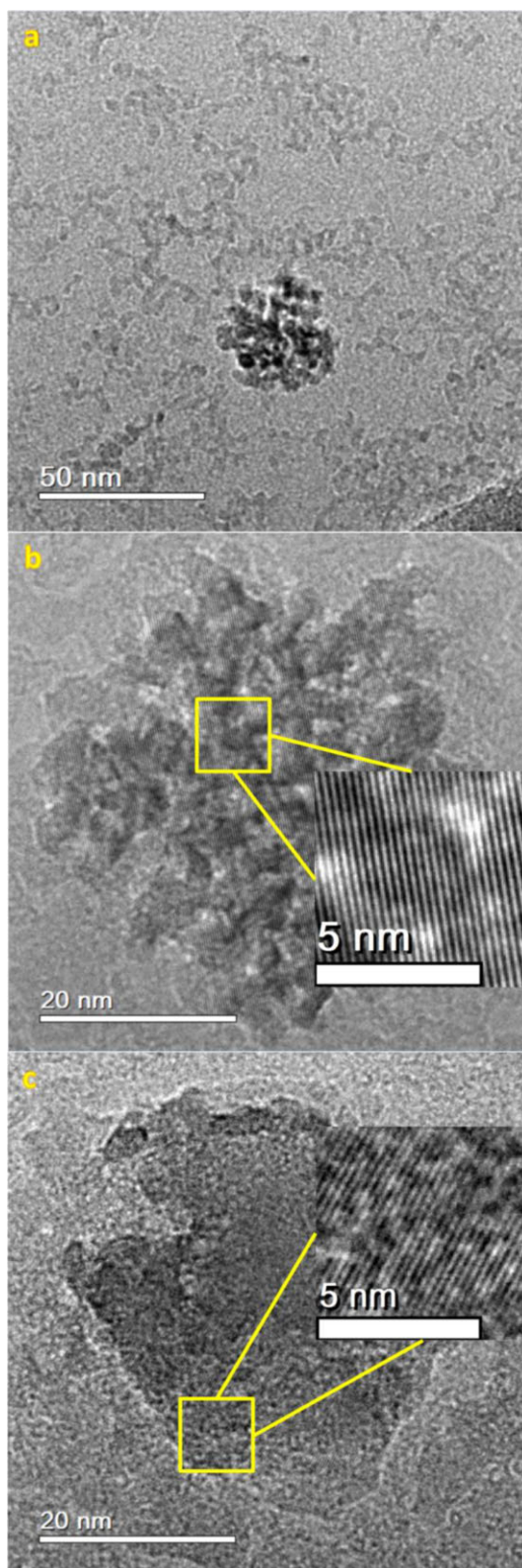


Fig. 2. TEM image (a) and HRTEM of the sample FhAl-10% aged for 130 days at 30 °C showing the hematite mesocrystal (b). HRTEM of the sample FhAl-0% aged for 130 days at 30 °C showing relatively euhedral hematite crystal (c).

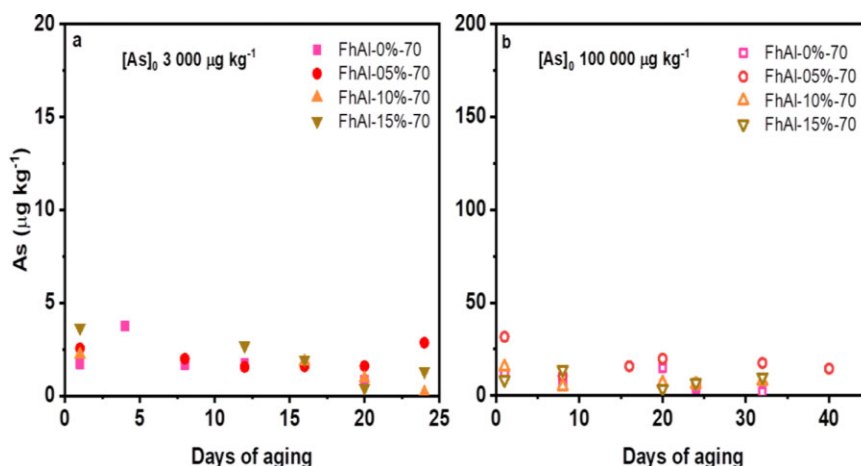


Fig. 3. Arsenic present in the supernatant during Fh aging, at 70 °C.

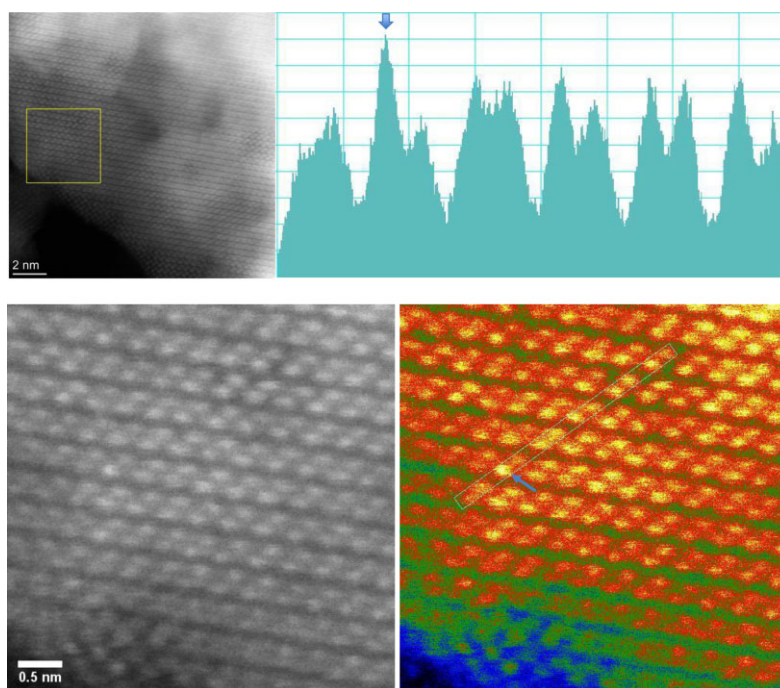


Fig. 3. HAADF-STEM image of FhAl-10% aged for 130 days at 30 °C showing the hematite mesocrystal. The bottom left image is a digitally magnified image of the area indicated in the top left image, where no significant thickness/mass contrast is present. To help visualize the Z-contrast of the atomic columns a temperature color table was applied to the image. Also, the line profile across a specific atomic plane shows an atomic column with a higher Z-number which can be due the presence of As in the particular atomic column.

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