



	Kinetics and mechanisms of Ni uptake by a nanocrystalline Mn oxide	Experiment number: eV-144
Beamline: ID22	Date of experiment: from: 29 th of January, 2015 to: 1 st of February, 2015	Date of report: 01/05/15
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Report:

This experiment aimed at determining the kinetics of trace metals sorption at nanocrystalline materials surface, taking the example of Ni interaction with vernadite, a nanocrystalline and defective Mn oxide which is ubiquitous in the environment. During the course of the experiment, a few reference samples were measured in sealed polyimide capillaries, while the very large majority of the beamtime was dedicated to the measurement of in-situ interaction of Ni with vernadite. In this view, we used a flow-through reactor, whose principle is shown in figure 1.

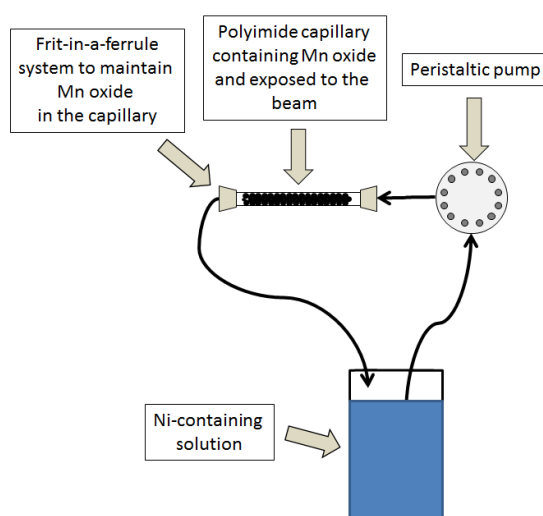


Figure 1. The experiment set up.

Experiments were run at different equilibrium pH values and different aqueous Ni concentration to increase our understanding of the impact of environmental conditions on the capacity of vernadite to uptake Ni. More specifically, data were acquired at pH 3, pH 5.6, pH 8.6 and pH 12. At pH 3 and 12, solutions

were left unbuffered. Contrastingly, at pH 5.6 and 8.6, data were buffered using a MES or a CHES pH-buffer, as pH was otherwise observed to drift during the experiment. Ni concentration in the input solution was $\sim 10^{-4}$ mol L $^{-1}$ for all experiments but the one conducted at pH 3 ([Ni] slightly less than 10^{-3} mol L $^{-1}$). For all experiments, a “blank” run (with all chemical parameters identical to the Ni experiment, but no Ni in solution) was performed, to ensure that structural modifications that would eventually be observed can be attributed to Ni. All experiments were successful, no leak or another problem occurred. Diffraction data were acquired up to $q \sim 250$ nm $^{-1}$, so that data can be Fourier-transformed to ultimately obtain X-ray pair distribution function data. This type of data is very useful to study sorption mechanisms, as studied minerals suffer from medium- to long-range disorder. During the course of the experiment, data were collected approximately every ~ 10 -15 seconds. 20 successive acquisitions were systematically averaged. Thus, an accurate determination of sample structure evolution with a time step of 5 minutes can be done.

Data processing and interpretation is ongoing. Almost all data were already successfully averaged, reduced to 1D data, and most of them have been transformed to pair distribution function (PDF) data. Data simulation will be performed using a structure model previously implemented using data from ID15 (Grangeon et al., 2015). Preliminary analysis of present data demonstrate that experiments were successful. Indeed, as exemplified here below with the example of the experiment conducted at pH 5.6, it can be observed that PDF data evolve as a function of time, some of the correlations increasing in intensity as a function of time, and others decreasing (Fig. 2a). The alternance of increasing and decreasing evolution proves that such evolution cannot be an artifact such as a varying amount of sample being exposed to the beam as a function of time (as it could have occurred if the solution has made the particles move in the capillary). After interpretation of the PDF data, it can be deduced that the modulations that effect the data can be interpreted in terms of progressive sorption of Ni above/below vacancies of the vernadite layers (Fig. 2b). Ongoing work consists in performing simulation of the data to quantify the amount of Ni that sorbs above the vacancies as a function of time, and in applying the same data treatment to all experiments that were performed.

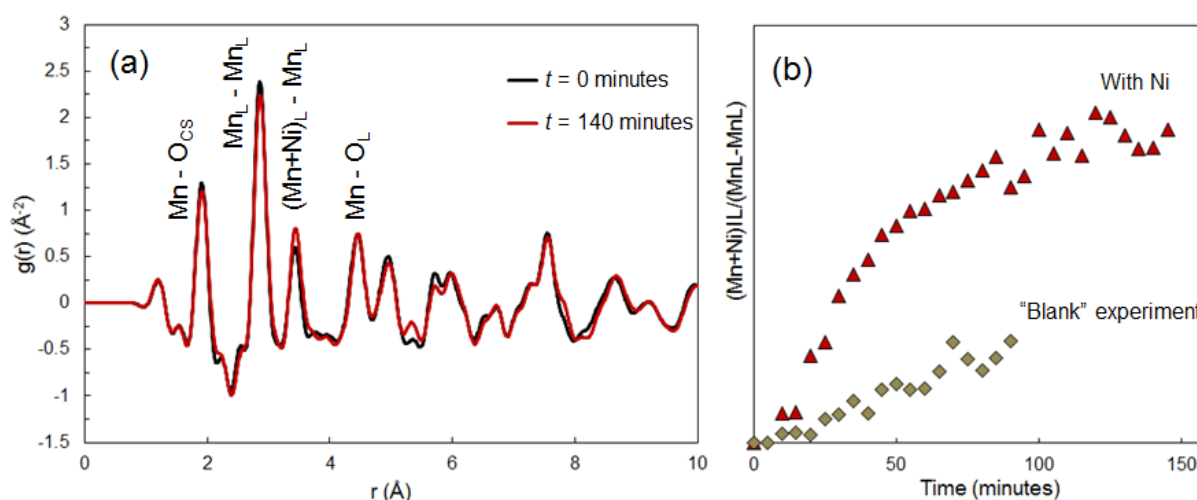


Figure 2. (a): Evolution of PDF data as a function of time in the experiment at pH 5.6 and in presence of Ni. Mn, Ni, O_{CS} , Mn_L , and $(Mn+Ni)_L$ respectively refer to Mn and Ni atoms (whatever their position in the structure), to oxygen from Mn or Ni coordination sphere, to layer Mn and to Mn and Ni interlayer species adsorbed above layer vacancies. Full indexation available in Grangeon et al. (2015). Thus, for example, $Mn-O_{CS}$ indicates an atomic pair formed by Mn and O from its coordination sphere, and Mn_L-Mn_L an atomic pair formed by two Mn atoms located in the vernadite layer (b): evolution of the intensity of the correlation involving interlayer Mn and Ni adsorbed above layer vacancies relative to that involving layer Mn. Thus, when this ratio increases, more Mn and (or) Ni are adsorbed above layer vacancies.

Reference

Grangeon, S., Fernandez-Martinez, A., Warmont, F., Gloter, A., Marty, N., Poulain, A., and Lanson, B. (2015) Cryptomelane formation from nanocrystalline vernadite precursor: a high energy X-ray scattering and transmission electron microscopy perspective on reaction mechanisms. *Geochemical Transactions*, 16(1), 12.