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135 - Tackling rapid reaction kinetics at the mineral-water interface using quick-scanning X-ray absorption spectroscopy

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Abstract: Reaction kinetics are extremely important for understanding basic chemical processes at soil mineral-water interfaces, such as sorption/desorption, oxidation/reduction, and precipitation/dissolution. These reactions can occur rapidly, and studies on the fast reaction kinetics has been challenging. The Sparks' group has been working on soil reaction kinetics for more than 30 years and pioneering new methodologies in this field. In 1980s, the group has developed stir-flow techniques and pressure-jump relaxation methods to investigate the mechanisms of rapid soil chemical reactions. Recently, the group published quick scanning X-ray absorption spectroscopy (Q-XAS) studies on Cr(III) and As(III) oxidation kinetics at a sub-second time-resolution. Despite the success of these methods, no method so far can provide time-resolved mechanistic information under dynamic, flow conditions in a short period of time in the EXAFS region. In this paper, we report the development of a novel method which couples a flow-cell with quick-scanning extended X-ray absorption fine structure spectroscopy (QEXAFS) to make the in-situ real-time measurement of geochemical reactions possible. Using QXAFS, we investigated Ni sorption reaction at the clay and Al oxides surface, and examined the rapid formation mechanisms of nickel (Ni) surface precipitates as layered double hydroxide (LDH) phases at the sorbent-solution interface. Research was conducted at beamline X18B of the National Synchrotron Light Sources (NSLS) at Brookhaven National Laboratory (BNL), with the monochromator set to the quick-scanning mode and oscillating at 0.5Hz. As a result, a single fluorescence EXAFS spectrum can be obtained in ~ 1s. The quick-scanning EXAFS experiments clearly indicated that the precipitates can form as rapidly as surface adsorption, i.e., less than 10 minutes on $\gamma\text{-Al}_2\text{O}_3$ and within 30 minutes on pyrophyllite. The data further revealed that a transition from surface adsorbed Ni to Ni-Al LDH precipitate formation occurred and no intermediate phases like Ni hydroxides formed. This research provides fundamental information for developing novel environmental remediation technology.