

Kinetics of Formation of Mixed Metal Hydroxides on the Surfaces of Clays

A. Scheinost¹, R.G. Ford¹, D. G. Strawn², G.M. Lamb^{3,4} and D.L. Sparks¹

¹Department of Plant and Soil Science, Townsend Hall, University of Delaware

²Department of Environmental Science, Policy and Management, University of California,

³Advanced Light Source Division,

⁴Earth Sciences Division,

Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720, USA

BACKGROUND AND INTRODUCTION

Recent time-resolved, traditional XAFS measurements made at the NSLS in studies by Donald Sparks' group at the university of Delaware made an important contribution to the understanding of metal ion retention in the environment[1][2][3][4]. It was found that, under certain conditions of pH and concentration, nickel forms nickel-aluminum hydroxides on the surfaces of a number of clays. These hydroxides are quite resistant to dissolution and being less soluble severely reduce the mobility of Ni in the environment. It is thought that the same behavior will apply to a large number of other metal contaminants; the main criteria being that the ionic radius should be reasonably close to that of the aluminum cations. It was found that, like many cation-mineral reactions, there was a very rapid rate in the first part of the reaction, which lasted about 25 minutes. This was followed by a much slower rate until the experiment was considered to be complete and the last measurement made after 250 hours. The rapid part of the reaction is usually attributed to adsorption and complex formation whereas the slow second part is generally thought to be due to the formation of surface precipitates or to the incorporation of the cation(s) into the bulk.

The measurements were made by exposing pyrophyllite clay to Ni ions in solution for a specific length of time and then washing immediately to assure that further reaction had been arrested. The sample was then measured using XAFS. Although, to our knowledge, this was the first time that such measurements had been made to obtain kinetic information using XAFS it was not possible to obtain analyzable data at metal/clay reaction times of less than 15 minutes. This is because the average concentration of Ni on the clay surface over the area of sample measured was too low to provide sufficiently good statistics to give speciation information.

The data analysis of the traditional XAFS data, including a full structural analysis suggested that the Ni was forming three-dimensional surface precipitates of nickel aluminum hydroxide. The X-Ray Fluorescence and the Micro-XAFS capabilities[5] at beamline 10.3.2 were used to take a closer look at the precipitates of these mixed metal hydroxides and their micro-structure, at shorter exposure times than it had previously been possible to measure.

RESULTS

XRFM measurements of one of the low coverage structures are shown in Figure 1. This particular pyrophyllite clay substrate had been exposed to Ni solution for ten minutes. It can be seen that some form of Ni aggregation or precipitation is already forming at these short reaction times.

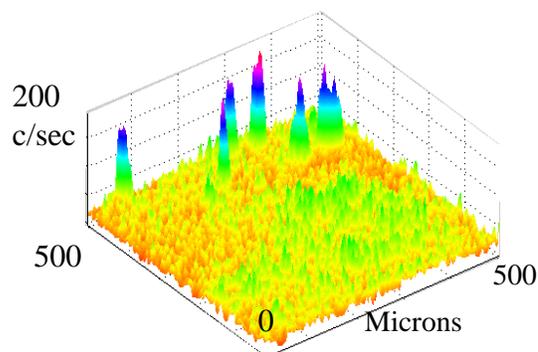


Figure (1) Map of Ni Kedge fluorescence for a low coverage phase (10 minutes reaction time of clay surface with Ni ions) showing regions of local concentration of Ni.

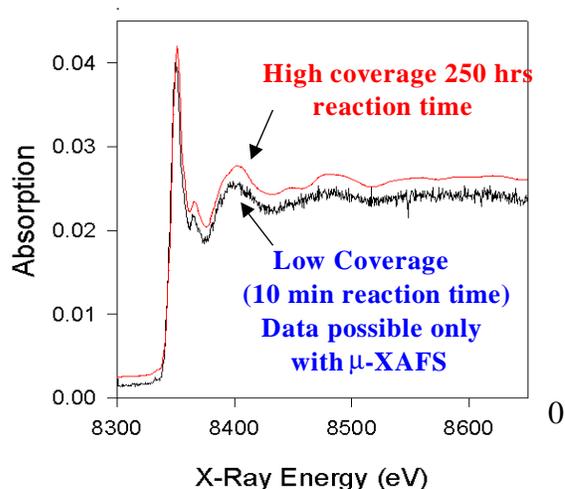


Figure (2) μ -XAFS measured in regions of local concentration, shown in (1). Results from the μ -XAFS indicate that the precipitates which begin to form at low coverage resemble those from the highest loading. This has important implications for the transport of low concentrations of contaminants.

It was possible to make μ -XAFS measurements on these precipitates which, after a 10 minute exposure to the Ni solution, appeared to be a few microns in size. This data are shown in Figure 2 along with data taken using the conventional technique of the longest reaction time (250 hours).

These initial data indicate that the precipitates formed at these low coverages are of similar type as those formed at the higher coverages. This suggests that the mixed-metal “binding” of contaminants occurs close to the onset of adsorption which, in itself, has important implications for metal transport in the environment. More extensive studies are planned [4] in order to check the reproducibility of these initial results. This particular example shows how, in the case where there is aggregation and thus local concentration on the micron scale, μ -XAFS can be more

sensitive than the macroscopic technique and why the parameter describing absorber ‘dispersion’ is more meaningful than the macroscopic value of the concentration.

References

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ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Principal investigator: Professor Donald L. Sparks, Department of Plant and Soil Science, Townsend Hall,
University of Delaware Plant and Soil Sci Phone (302) 831-2532 Email: dlsparks@udel.edu