The formation and oxidation of green rust: Mechanisms, kinetics and trace element speciation

G. KAKONYI, S. SHAW, I.A.M. AHMED AND
L.G. BENNING

School of Earth and Environment, University of Leeds, Leeds, UK (g.kakonyi@see.leeds.ac.uk)

Green rust (GR, $Fe^{2+}{}_4Fe^{3+}{}_2(OH)_{12}$-$SO_4 \cdot xH_2O$) nanoparticles have the potential to provide effective solutions for contaminated groundwater remediation (e.g., permeable reactive barriers). Structural Fe^{2+} within GR can reduce adsorbed trace elements (e.g., Se^{6+}) and significantly lower their solubility and bioavailability. GR forms in suboxic environments and when exposed to oxic conditions rapidly transforms (minutes) to various iron (oxyhydr)oxide phases. The kinetics and mechanisms of these reactions and the fate of associated trace elements are poorly understood.

Synchrotron-based *in situ* time-resolved Small/Wide Angle X-ray Scattering (SAXS/WAXS) and Energy Dispersive X-ray Diffraction (EDXRD) were used to characterise the crystallisation and oxidative transformation of GR nanoparticles via the oxidation of a Fe^{2+}-sulphate solution, utilizing advanced environmental cells. The speciation of associated trace elements (i.e., Zn and Se) were analyzed by X-ray Absorption Spectroscopy (XAS). Results showed that initially $Fe(OH)_2$ formed which then transformed to GR-sulphate (GRII). With continued oxidation GRII transformed to lepidocrocite (L) and goethite (G) (Fig. 1).

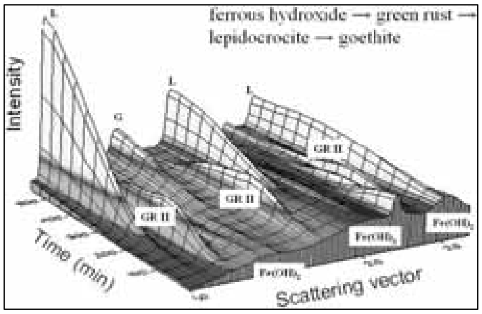

Figure 1: Time-resolved WAXS data showing GR formation and transformation.

The EDXRD showed that with increasing pH (pH 7, 8, 9) the rate of GRII transformation and the final L/G ratio increased. Zn^{2+} replaces Fe^{2+} in the structure of GRII, and retards the oxidative transformation by ~50%. XAS data indicates that Se^{6+} is reduced during GR formation, but only partially reoxidised when transformation to lepidocrocite/goethite occur.

Librational dynamics of nano-confined water: Neutron spectroscopy and molecular dynamics computer simulations for hydrocalumite

A.G. KALINICHEV[1], A. FARAONE[2,3], T.J. UDOVIC[3],
A.I. KOLESNIKOV[4], N. R. DE SOUZA[4], M.X. REINHOLDT[5]
AND R.J. KIRKPATRICK[6]

[1]Department of Chemistry, Michigan State University,
East Lansing, MI 48824 (kalinich@chemisry.msu.edu)
[2]Department of Materials Science and Engineering, Univeristy of Maryland, College Park, MD 20742
3NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899
4Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, IL 60439
[5]Département de Génie Chimique, Université Laval,
Cité Universitaire Québec (QC) G1K 7P4 Canada
[6]College of Natural Science, Michigan State University,
East Lansing, MI 48824

Molecular-scale understanding of the structure, dynamics, and energetics of nano-confined water in mineral interlayers and nano-pores is essential for many geochemical, environmental and technological applications. Layered double hydroxides (LDHs) are excellent model systems for such molecular-level studies, because their interlayers have a well-defined structures and can contain H_2O molecules and various anions in well-defined structural positions.

Here we report the first results of a comprehensive investigation of the H_2O structure and dynamics in the interlayers of hydrocalumite – an LDH phase with the composition of $[Ca_2Al(OH)_6]Cl \cdot 2H_2O$. One fully hydrated and one dehydrated sample were studied by the inelastic and quasielastic neutron scattering techniques using several complementary instruments (HFBS, DCS and FANS at NCNR; HRMECS and QENS at IPNS) at temperatures above and below the previously discovered phase transition.

Together the experimental and molecular modeling results capture the important details of the dynamics of nano-confined water and the effects of the orientational ordering of H_2O molecules above and below the phase transition. They provide otherwise unobtainable experimental information about the transformation of H_2O librational and diffusional modes across the order-disorder phase transition and significantly add to our current understanding of the structure and dynamics of water in LDH phases based on the earlier NMR, IR, X-ray, and calorimetric measurements.