

Ion exchange in fougèrite: influence of crystal size and structural defects

M.I. AGNEL^{1*}, S. GRANGEON², F. FAUTH³, E. ELKAÏM⁴,
F. CLARET², M. ROULET⁵, F. WARMONT⁵, C.
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¹ ISTO, UMR 7327 Université d'Orléans/CNRS/BRGM,
45071 Orléans, France (correspondence:
myriam.agnel@cnrs-orleans.fr)

² BRGM, 45060 Orléans, France

³ CELLS – ALBA Synchrotron, 08290 Barcelona, Spain

⁴ Synchrotron SOLEIL, 91190 Saint Aubin, France

⁵ ICMN, UMR 7374, CNRS/Université d'Orléans, 45071
Orléans, France

⁶ Energy Geoscience Division, Lawrence Berkeley National
Laboratory, Berkeley, CA 94720, USA

Fougèrite is a Fe(II)/Fe(III) layered double hydroxide found in hydromorphic soils. Its layers are positively charged because of the occurrence of mixed Fe^{2+/3+} valence states. The charge is compensated by exchangeable anions located in the interlayer space. Consequently, fougèrite, where present, participate to the biogeochemical cycling of anions, including nutrients or pollutants, in the environment. In this study, we carried out a detailed analysis of some of green rust (GR, synthetic fougèrite) ion exchange properties.

We investigated the Cl⁻/SO₄²⁻ exchange mechanism on two samples having similar layer structures, but different particle size: nanometric or micrometric size range particules. Samples were characterized by synchrotron high-energy X-ray scattering and synchrotron in situ and time-resolved X-ray diffraction. Total anion exchange capacity and Cl⁻/SO₄²⁻ selectivity coefficients (K_{ex}) were obtained from modelling of aqueous chemistry data and microprobe analyses.

The replacement of Cl⁻ by SO₄²⁻ followed a 2:1 stoichiometry, and led to an increase of interlayer distances from $8.3 \pm 0.1 \text{ \AA}$ to $11.3 \pm 0.1 \text{ \AA}$. No dissolution or recrystallization reactions were observed. An increase of SO₄²⁻ occupancy in the interlayer led to an increase of the relative affinity of the exchanger for SO₄²⁻ compared to Cl⁻. Exchange data were adequately described with an anion exchange thermodynamic model using the Rothmund-Kornfeld convention. The model parameters were different for the nanometric GR particles and the micrometric GR particles, evincing a higher affinity of SO₄²⁻ for the nanometric sample. This difference of affinity may originate from differences in layer stacking order in the two types of samples, the nanometric particles being turbostratic while the micrometric particles being 3D-ordered.