

Fate of Sorbed Arsenic during Aging and Transformation of Green Rust

C. M. VAN GENUCHTEN,^{1,2} T. BEHRENDTS,¹ S.L.S. STIPP,^{2,3} K. DIDERIKSEN^{2,4}

¹Faculty of Geosciences, Utrecht University, NL
c.m.vangenuchten@uu.nl

²Nano-Science Center, University of Copenhagen, DK

³Physics, Danish Technical University, DK

⁴GEUS (Geological Survey of Denmark and Greenland), DK

Green rusts (GRs) are Fe(II,III) hydroxides that consist of sheets of edge sharing Fe(OH)₆ octahedra with interlayer water and anions (e.g. Cl⁻, SO₄²⁻, CO₃²⁻). The abundance of reactive sorption sites on GR particle edges makes these minerals ideal candidates for implementation in remediation of water and soils contaminated by arsenic (As). Depending on aging and solution conditions, GRs can be metastable, transforming readily into other Fe minerals, such as lepidocrocite and magnetite. While GR has been shown to be an effective sorbent for As, less is known about the fate of As, such as release to solution, changes in oxidation state and sorption configuration, when GR transforms during aging.

In this work, we generated carbonate green rust (GR-CO₃) in the presence of arsenate (As(V)) or arsenite (As(III)) and aged the suspensions in anoxic and in oxic conditions. The aqueous As concentration during GR aging was measured after an hour, a day, a month and a year and the Fe and As speciation was tracked with Fe and As K-edge X-ray absorption spectroscopy.

Aqueous As concentrations increased from 14±8 to 69±20 µg/L when As(V)-sorbed GR-CO₃ aged anoxically for 1 month. Anoxic aging for a year resulted in a decrease in aqueous As to <2 µg/L, which coincided with transformation of the initial GR to magnetite and transition from As(V) adsorbed to GR edges in binuclear, corner sharing (²C) geometries to As(V) in the tetrahedral iron sites of magnetite. When aged in oxic environments, As(V)-sorbed GR-CO₃ transformed rapidly (<1 hour) to lepidocrocite, which decreased dissolved As to <1 µg/L. During oxic aging, As(V) remained adsorbed to the solids and did not incorporate into the lepidocrocite structure. Similar trends were observed with As(III)-laden GR suspensions, but the anoxic transformation to magnetite was considerably faster (1 day) than for As(V)-sorbed GR (>1 month). Our results indicate that GR aging to form magnetite (anoxic) or lepidocrocite (oxic) decreases dissolved As, but the As retention mechanism varies depending on the aging product. These results improve our understanding about the long term behaviour of As in varying redox conditions, which is essential for accurate predictions of aqueous As in natural and engineered systems.