Biomineralization of Fe^{II}-Fe^{III} green rust in γ-FeOOH coated sand column under saturated flow conditions

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The synthesis of Fe(II)–Fe(III) green rusts (GR) in environmental and engeneering systems is a challenging project due to the higher reactivity of GR towards a panel of organic or inorganic pollutants. While the biomineralization and stabilization of GR have been well described in batch reactor from ferric oxide respiration by *Shewanella putrefaciens* [1, 2] or mixed cultures of bacteria [3, 4], their formation routes as a main secondary iron mineral under flowthrough conditions remain undescribed.



Figure 1: Picture of a green rust (GR) crystal obtained in a lepidocrocite (L) sand packed column incoculated with *S*. *putrefaciens* and fed with formate as electron donor.

Formation of both GR and magnetite was observed in a lepidocrocite-coated sand packed column at a flow rate of 0.1 mL/min. However, GR was the dominant secondary mineral when silicate was present in the injected feed solution (Fig.1). In this latter case, untransformed lepidocrocite was still present in the sand packed column. This behavior could be explained by the sorption of dissolved silicate on the lepidocrocite surface, which might hinder the reactive sites and so limit the bioreduction extent. On the other hand, the interactions of dissolved Si with the lateral faces of the GR crystals could stabilize the GR structure, thus preventing its transformation into magnetite.

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Hg (II) sequestration by ettringitetype phases. A geochemical modeling and EXAFS study

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Sequestration of Hg by ettringite-type phases (Ca₆ [Al (OH)₆]₂ (SO₄)₃26H₂O), formed during hydration of Portlandtype and super-sulfate cements, as a potential method for sediment remediation was investigated theoretically with a kinetic-equilibrium model and experimentally in coprecipitation (Hg+Al+SO₄+Ca and Hg+Fe+SO₄+Ca systems) and substrate-amended (quartz, clay, and/or sediment) batch experiments in aqueous NaCl solutions. Geochemical modeling predicted formation of ettringite and calciumsilicate-hydrate (C-S-H) gels as a function of reaction time, corroborating XRD results for amendment batch experiments. XRD patterns of the co-precipitation products showed Alettringite and gypsum as the main mineral phases in the Hg+Al+SO₄+Ca and Hg+Fe+SO₄ +Ca systems, respectively. Extraction results indicated that <20% of added Hg was associated with the exchangeable fraction in both coprecipitation and substrate-amended batch experiment. XAS and electron microprobe characterization of the Hg coprecipitation and cement hydration products suggests physical micro-encapsulation of Hg in ettringite as a polynuclear chloromercury calcium precipitate. Hg XAS analysis of the solid products in the Hg+Fe+SO₄+Ca system indicated Hg sorption on ferrihydrite as the main retention mechanism. These results revealed that, in the presence of Cl-, Hg immobilization in cement systems is kinetically controlled by Hg-Cl complexation and precipitation of cement hydration products. However, in high Fe systems, Hg retention predominantly as the Hg (OH)₂ species, is controlled by fast sorption equilibrium on ferrihydrite.

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